APTD-1174

PB 210 822

DEVELOPMENT AND EVALUATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF TOTAL ATMOSPHERIC MERCURY

FINAL REPORT

Covering the Period
November 1970 Through March 1972

Contract No. EHSD 71-32

Prepared for: Environmental Protection Agency
Division of Atmospheric Surveillance

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June 16, 1972

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BIBLIOGRAPHIC DATA SHEET	1. Report No. APTD-1174	2.	3. Recipient's Accession No. PB-210 822
4. Title and Subtitle: Development and Evaluation of an Analytical Method for the Determination of Total Atmospheric Mercury			5. Report Date: June 16, 1972 6.
7. Author(s): D. L. Chase, D. L. Sgontz, E. R. Blosser, W. M. Henry			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: BATTELLE, Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201			10. Project/Task/Work Unit No. 11. Contract/Grant No. EHSD 71-32
12. Sponsoring Organization Name and Address: ENVIRONMENTAL PROTECTION AGENCY, Division of Atmospheric Surveillance, Research Triangle Park, North Carolina			13. Type of Report & Period Covered: Final 14.

15. Supplementary Notes

16. Abstracts

Total mercury in ambient air can be collected in iodine monochloride, but the subsequent analysis is relatively complex and tedious, and contamination from reagents and containers is a problem. A silver wool collector, preceded by a catalytic pyrolysis furnace, gives good recovery of mercury and simplifies the analytical step. An instrumental method based on particle counting proved unreliable, but another instrument using the 253.7 nm Hg optical absorption line proved to be quite accurate for the determination of elemental mercury in air.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Chemical analysis
Mercury
Iodine inorganic compounds
Chlorides
Silver inorganic compounds
Catalysis
Pyrolysis
Spectrophotometry

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13B

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Unlimited	UNCLASSIFIED	73
	20. Security Class (This Page) UNCLASSIFIED	22. Price $5.75

FORM NTIS-35 (10-70) USCOMM-DC 40329-P71

MANAGEMENT SUMMARY

Contract No. EHSD 71-32

"Development and Evaluation of an Analytical Method to Determine Total Atmospheric Mercury".

Objective of Research Program

This program was initiated to develop a method for determining mercury, both organic and inorganic, in ambient air. It was directed first to systems using iodine monochloride as a collecting medium and later was broadened to include other mercury collection and measuring systems.

Significance of Research Results

The research data show that the chemical absorption method involving iodine monochloride, while capable of collecting various forms of mercury and therefore valuable in certain respects, presents severe contamination and analytical problems. A pyrolysis-amalgamation technique appears to be quite useful and reliable for many, if not all, forms of mercury and is amenable to straightforward chemical analysis as well. Two commercial instruments were evaluated; one appeared valid for elemental mercury vapor, but the other was unreliable.

How Sponsor Can Use Results

The Environmental Protection Agency will be able to use the information generated in this research program to guide it in the development of an analytical system for monitoring the air for mercury content.

Future Effort

Additional research effort is outlined that could provide more basic information about the iodine monochloride system. Also additional research effort could be useful in providing more precise operating conditions for the pyrolyzer-silver wool system.

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DEVELOPMENT AND EVALUATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF TOTAL ATMOSPHERIC MERCURY

by

D. L. Chase, D. L. Sgontz, E. R. Blosser, and W. M. Henry

SUMMARY AND RECOMMENDATIONS

Iodine monochloride is an effective collection medium for the several chemical forms of mercury, providing the rate of air flow is kept sufficiently low to permit an adequate reaction time between the ICl and organometallic mercury. The actual determination of the mercury so collected may be made by a dithizone extraction or by aeration techniques. Double aeration is preferable to eliminate possible interferences from the ICl solution. Electrodeposition or coprecipitation of mercury from ICl solutions are not satisfactory. The ICl collection and subsequent dithizone extraction and/or double aeration methods are too tedious for the rapid analysis of large numbers of samples and may not provide satisfactory accuracy for mercury contents of air in the nanogram range.

Of two commercial instruments designed to determine ambient air mercury, one proved unreliable while the other (primarily a collection system), under limited evaluation gave satisfactory data on elemental mercury for several simulated samples.

It is recommended that the ICl absorber system not be adopted in its present state of development for universal use in mercury collections owing to the somewhat difficult (dithizone) and unreliable (reduction-aeration) analytical procedures required, plus lack of sensitivity and high blank. It is a suitable collection medium if necessary precautions are observed and if above-average analysis time and if a detection limit of about 1 ng Hg/m^3 can be tolerated.

The adoption of one commercial instrument for the determination of mercury is not recommended at least in its present form. Insufficient data were available

on this program to permit a thorough judgment of a second commercial instrument, but the data available are favorable for its application to determining elemental mercury in air.

The pyrolysis-silver wool system appears to be the best collection method yet devised for total atmospheric mercury. It has shown no interferences in work to date; it is capable of collecting elemental, particulate, and organometallic forms of mercury; and it collects the mercury in a form suitable for easy, rapid analysis. Pending further evaluation and field testing, it is recommended that this system receive favorable attention and research effort.

INTRODUCTION

In the mounting concern with environmental quality many formerly unsuspected hazards have emerged, usually with widespread publicity and accompanied by alarmist overstatements of the danger. Mercury, widely used by industry and by consumers in relatively small amounts, finds its way into the air, the soil, and the water by many routes. Natural losses such as evaporation and leaching also contribute to the mercury cycle.

One of the first requirements in evaluating the extent of man's impact upon the mercury cycle (or any other environmental stress, for that matter) is accurate analytical data. The Environmental Protection Agency, charged by law and executive order with gathering these data, setting standards, and overseeing enforcement of regulations, is studying means to assure that the data upon which decisions must be made are valid and accepted by those concerned.

Mercury is a heavy and toxic element that exists in the atmosphere as an element, as a gaseous compound, and as a particulate. Its chemistry is such that many of the usual means used to collect samples for analysis fail to collect all the mercury present. Furthermore, the volatility and instability of some forms of mercury make the retention of mercury difficult unless

special precautions are taken. For these reasons several systems have been devised that will catch and retain the important known forms of mercury.

One such method, using a solution of iodine monochloride (ICl), has been reported to be effective in removing different forms or chemical species of mercury from air.[20]* The present program had as one of its primary objectives the development of a reliable method to analyze ICl solutions in which had been collected the mercury from air samples. As the program progressed, other collection schemes and other analytical methods were also explored.

During the course of this program the emphasis of the research effort was altered several times when difficulties were encountered, when new developments elsewhere came to the attention of EPA, and when expediency dictated that a particular technique be studied in a short time. In this report the experimental work and results are presented topically as much as possible, rather than chronologically. Reference is made to the monthly report(s) in which the work was reported; however, the technical details are described fully in this report.

EXPERIMENTAL WORK

Preparation of Working Mixtures, Solutions, and Standards

Working dilutions (solutions, air mixtures, or standards) of mercury were prepared in two basic ways: (1) by the direct addition of a known volume of a solution of a mercury compound, and (2) by the addition of a known quantity of mercury (elemental or compound) by aeration, volatilization, or permeation into an inlet air stream, a collector, or the atomic absorption cell. The two approaches are described in the following sections.

Direct Addition

Several series of standards containing known amounts of mercury were prepared daily by adding suitable aliquots of aqueous $HgCl_2$ in 0.1 M HCl to ICl solutions.[1]

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* References are listed at the end of the report.

This direct method, carefully carried out, should be quite free from any bias errors except the usual inaccuracies of weighing and measuring, and was used as a means of preparing reference solutions for several experiments. These solutions are only stable at ppm or higher concentrations and should not be stored in plastic ware.

Aeration

Aeration is only slightly less direct than the preceding direct addition method, and it has the advantage that a known amount of mercury vapor (elemental) is produced and can be absorbed in an impinger or introduced directly into a readout chamber such as the absorption cell in the atomic absorption unit. The aeration method, employed to check out several of the analytical procedures[2,5,6,17], is based on the reduction of Hg^{++} to Hg° in solution and subsequently sweeping the Hg° vapor from the solution with a stream of air (or inert carrier gas, if desired)*.

Vaporization

This technique lends itself to a somewhat easier time-quantity control of the released mercury. A known quantity of a mercury compound is placed, in solution, into a vaporizing chamber such as shown in Figure 1[4] and Figure 2[13,19]. In practice, the desired amount of the mercury compound is pipetted into the vaporizing chamber which is promptly attached to the system and isolated. Proper manipulation of the stopcocks and vacuum pump gives a steady flow of air through the vaporizer, sweeping the mercury compound into an impinger or other collection or readout device. Vaporization, in common with direct introduction and aeration methods, provides good control over the total quantity of mercury introduced, but poor simulation of a steady-state mercury loading as is encountered in nearly all ambient air sampling conditions. Also, the small amount of residual solvent for the mercury compound may interfere with the subsequent analysis as, for example, the toluene used to dissolve dimethyl mercury interferes with the direct flameless atomic absorption determination of mercury.

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* We can neither confirm nor refute the reported variation between aeration and Hg vapor pressure calibration techniques described by Muscat, et al (Anal. Chem. 44, No. 2, p 218 (1972).

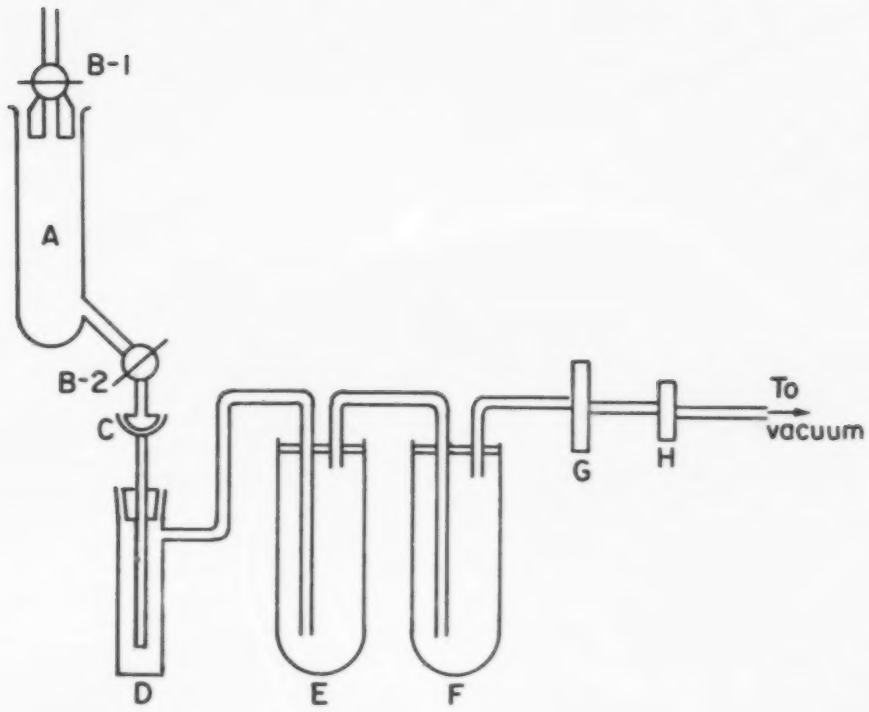

FIGURE 1. MERCURY IN AIR CALIBRATION ASSEMBLY

(A)	Vaporizer
(B-1 and B-2)	Teflon stopcocks
(C)	Ball joint
(D)	Impinger
(E)	Thiosulfate scrubber
(F)	Charcoal trap
(G)	Particulate filter
(H)	Manifold containing limiting orifice

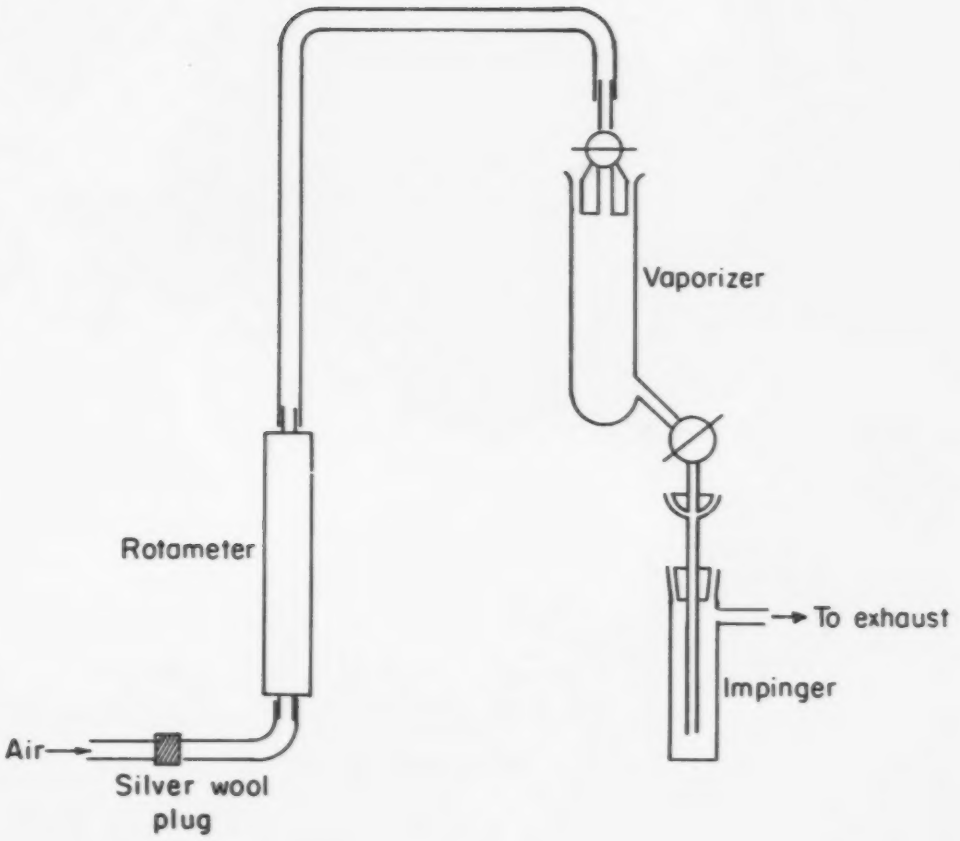

FIGURE 2. VAPORIZER ASSEMBLY

Permeation Tube

Permeation tube techniques are used to introduce known amounts of a substance into a gas stream at a constant rate. A tube is fabricated by placing the desired material in a semipermeable tube and sealing the ends.[21] The rate of permeation is a function of temperature as well as of the physical dimensions and characteristics of the tubing walls, but for reasonable time periods is not dependent upon the total amount of the material remaining in the tube. In this program some difficulty was encountered in constructing tubes with permeation rates suitable for use in preparing simulated gas samples. For two experiments in this program permeation tubes were used: mercury vapor was permeated through a silicone rubber tube for evaluation of a mercury sensing instrument[10] and for evaluating a collector system[17]. The design of the assembly is shown in Figure 3.[10,17]

ICl Experiments

Iodine monochloride (0.1 M, 0.5 N HCl) was chosen by EPA as a collection media for total atmospheric mercury using liquid impingers; the development of an analytical method to determine the mercury so collected was the initial purpose of this program. The solution could be analyzed directly using a flame-atomic absorption technique, but severe problems would arise owing to the corrosive nature of the solution, the (relative) insensitivity of the technique, and probable interference from free-iodine vapor. Therefore, several alternative methods were explored.

Electroplating

A series of solutions containing 0, 5, 10, and 15 nanograms of mercury as $HgCl_2$ in 40 ml portions of 0.1 M ICl was prepared. These solutions were electrolyzed at 3 volts for 20 minutes with a copper coil as the cathode and a platinum wire as the anode. After the plating step was completed the coils were washed in water, ethanol, and acetone, then dried and positioned in an absorption

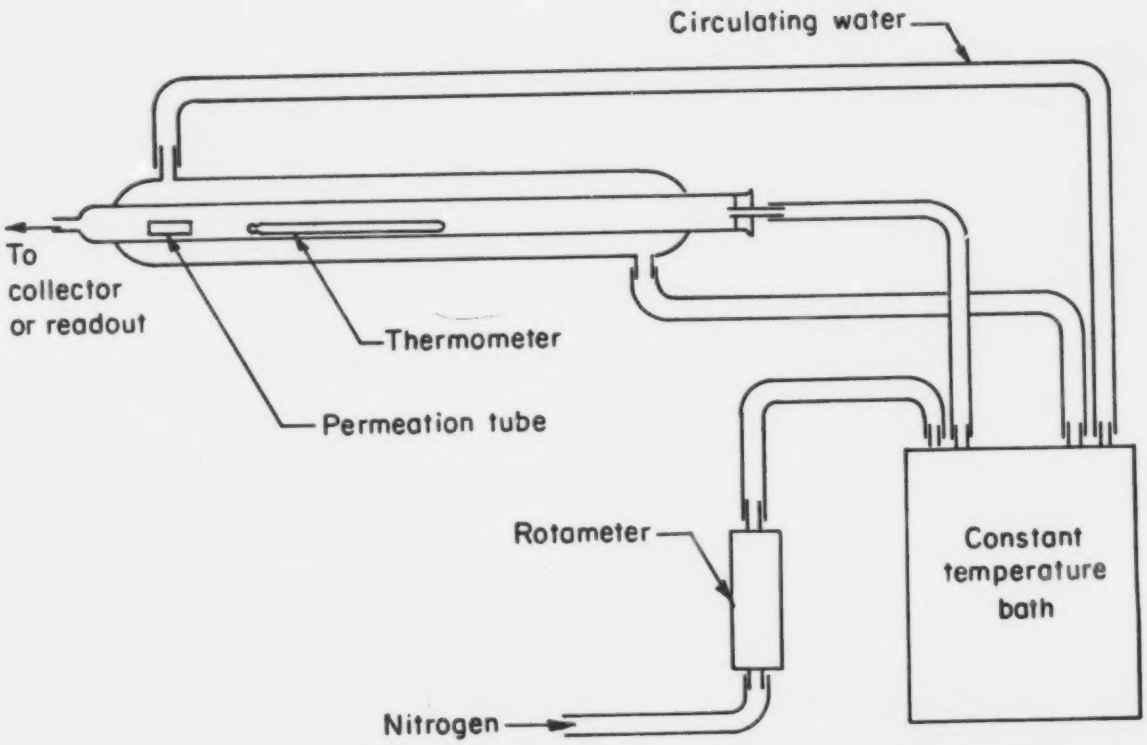

FIGURE 3. PERMEATION TUBE ASSEMBLY

cell mounted in the light path of the Perkin Elmer Model 303 atomic absorption spectrophotometer (AAS). A 5-volt current was passed through each coil to heat the wire and release the monoatomic mercury vapor for measurement by ultraviolet light absorption at 253.7 nm.[22]

All of the coils, including the blank, gave off a small cloud of smoke when heated, making accurate measurement of the mercury vapor impossible. On close inspection the coils were found to be covered with a thin deposit of a salt-like material (possibly a copper-iodine compound) that could not be washed off. Plating from an ICl solution which had been reduced by sodium thiosulfate produced the same type of deposit. These experiments indicated that the direct plating of mercury from ICl solutions onto inexpensive copper coils is impractical.[1]

Dithizone Extraction

One of the proposed methods to determine the mercury collected in ICl is to extract this mercury with dithizone using the procedure described by Linch, et al[20]. To evaluate this technique, several preliminary experiments were performed.

A simple flow-through aeration system was constructed and attached to the absorption cell placed in the light path of the Perkin-Elmer 303 atomic absorption spectrophotometer (AAS).[2] A series of standards containing 0, 5, 10, 15, and 20 nanograms of mercury as $HgCl_2$ in 50 ml of 2 N HCl was prepared. These standards were analyzed for mercury content by placing them individually in the aeration cell, reducing with stannous chloride solution, and pulling air through the system at about 1.0 liter per minute. Results were very encouraging. The response was good, blanks were relatively low, and readings were reproducible.

Having established that Hg^o could be aerated from an HCl solution into the AAS successfully, the extraction by dithizone of mercury from HCl, followed by aeration, was attempted. The method is based on a dithizone extraction from an HCl solution, back extraction into another HCl solution followed by aeration and

measurement. However, when the method was applied to a series of standards identical to those used to check out the flow-through aeration system, the recoveries were low and erratic. A study of the system showed that longer contact time was needed in both the dithizone extraction and back-extraction steps. At least 5 minutes shaking time was required in both steps to obtain reasonable recoveries of mercury. When these precautions were taken, the results with the HCl system were promising enough to try out the method on standards containing ICl.

A series of standards containing 0, 5, 10, 15, and 20 nanograms of mercury in 50 ml of the ICl collecting solution were prepared. The dithizone extraction and back extraction into 5 N HCl were carried out, using the 5 minute shaking time indicated by the previous experiments. When the final HCl solutions were reduced and aerated, the response obtained with all of the solutions was erratic. The blank was quite high , and the readings obtained from standards containing different levels of mercury were all high and roughly the same. This suggested the possibility that the KI and/or KIO_3 used to make up the absorbing solution contained mercury, or that some vapor other than mercury vapor was being swept into the absorption cell and absorbing ultraviolet light.

Analysis of Reagents. Samples of reagent grade KI and KIO_3 used to make up the ICl, as used as atmospheric sample collecting solutions in this study, were analyzed for mercury by a neutron activation technique.[3] The results of this analysis showed that the KI contained 0.1 ppm Hg and the KIO_3, 0.3 ppm Hg. Since approximately 0.555 g KI and 0.375 g KIO_3 were present in the diluted atmospheric sample absorbing solution, a blank of about 170 nanograms of Hg was being introduced by these reagents. This was unacceptable for the purpose of this collecting system and necessitated efforts to reduce the blanks to a more reasonable concentration.

Preparation of Purified Reagents. Initial efforts to purify the reagents followed a technique described by Monkman, et al.[23] CdS pads were prepared by treating a glass filter pad with 10 percent cadmium acetate and 10 percent sodium sulfide solutions alternately, beginning and ending with the cadmium acetate solution. The pad was then washed with water, pumped dry, and placed in an oven at 100° C for one hour. Finally the pad was heated in a muffle furnace at 375°C for one hour and stored in a desiccator until used. Small disks to fit the filtering apparatus were then cut out of the pad with a cork borer.

A solution containing 11.1 g KI in 200 ml of water and another solution containing 7.5 g KIO_3 in 200 ml of water were prepared. Each solution was filtered through a CdS pad. By adding 45 ml HCl to the filtered KI solution, adding the filtered KIO_3 solution, and diluting to 1 liter with water the diluted form of the ICl collecting solution was obtained. The mercury content of this solution was checked by adding an excess of NaOH to a 50 ml aliquot, reducing with hydroxylamine hydrochloride, and aerating through the absorption cell of the AAS. A comparison of the responses from the treated and untreated collecting solutions indicated that the mercury level had been lowered from about 150 nanograms to 10-15 nanograms in a 50-ml aliquot.

Unfortunately, the overall dithizone extraction procedure is lengthy and ill-suited to a large number of samples. By mutual agreement with the Project Monitor work on the extraction method was suspended indefinitely, even though it remains a method of demonstrated validity. As mentioned below, the dithizone extraction was employed to check some surprisingly high mercury values obtained in the analysis of submitted air samples and to check the glass impinger-ICl collection system.

Coprecipitation of Mercury on CdS

The coprecipitation of HgS and CdS by filtering a sample solution adjusted to pH 5-6 through a CdS pad forms the basis for a sensitive method for the determination of mercury.[23] The CdS pad containing the separated mercury is dried and placed in a tube furnace heated to 550° C to release mercury vapor. Air is drawn through the combustion tube to sweep the mercury vapor into an optical cell where the amount of ultraviolet light absorbed by the mercury vapor can be measured. This method was evaluated as a technique to be used for the determination of mercury in atmospheric sample absorbing solutions containing ICl.

An electric combustion furnace was fitted with a 25-mm-diameter Vycor combustion tube which tapers to a 7-mm diameter at one end. The constricted end was connected to the absorption cell of the AAS with rubber tubing. A pump was connected to the exhaust end of the absorption tube in order to draw air through the whole assembly. A series of standards containing 0, 10, 20, and 40 nanograms of mercury were prepared by adding 0, 10, 20, and 40 microliter aliquots of a standard 1μgHg/ml solution of mercuric chloride in acetone to CdS pads. A microsyringe was used for measuring the standard solution. These standards were dried and then placed, one by one, in a quartz boat which was inserted into the combustion tube heated to 550° C. Air was drawn through the system at about 1 liter per minute. The response of the atomic absorption spectrophotometer versus mercury concentration was linear and a satisfactory calibration was achieved as shown in Figure 4, Curve A.

The coprecipitation method was then applied to a series of standard solutions containing 0, 10, 20, and 40 nanograms of mercury in dilute HCl. These solutions were adjusted to pH 6 and filtered individually through CdS pads. The pads were dried and processed in the same manner as described above. Again the response was linear and a smooth calibration curve, closely matching curve A in Figure 4, was constructed for this set of conditions.

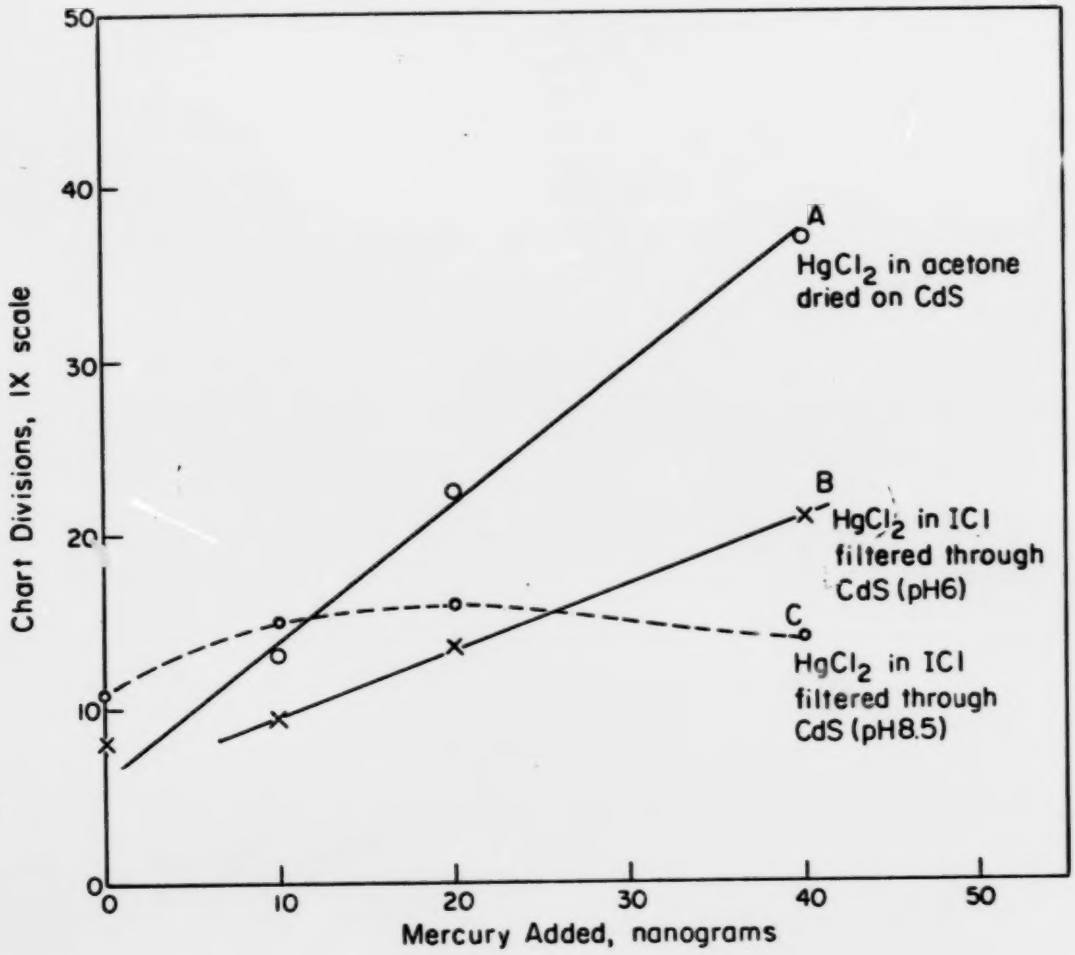

FIGURE 4. RESPONSE PLOTS FOR CdS COPRECIPITATION EXPERIMENTS

Standard solutions containing 50 ml of the purified ICl absorbing solution and 0, 10, 20, and 40 nanograms of mercury were prepared. These solutions were neutralized with NH_4OH to pH 6 and filtered through CdS filter pads. The pads were dried, transferred to small quartz boats, and heated individually in the furnace assembly described above. The blank at pH 6 was appreciable, equivalent to about ~ 15 ng Hg. Also, the slope of the curve (Figure 4, Curve B) was lower, indicating a possible suppressant effect or a partial (proportional) failure to achieve the complete precipitation of mercury by the CdS. This experiment was repeated with all conditions the same except the solutions were adjusted to pH 8.5 before filtering through the CdS pads. The response from the blank and standards was essentially the same as shown in Curve C, Figure 4. Another possible explanation of the failure to recover mercury is that it is tied up in a strong covalent iodide complex (HgI_4^{2-}) at pH 6 and is not available to react completely with the sulfide ion. At pH 8.5 the mercury is released from the complex but does not form a sulfide in this strongly alkaline medium. Of course these observations are based on very limited data.

On the basis of these limited experiments the coprecipitation method, while applicable to HCl solutions, does not appear to be suitable for the determination of mercury in ICl solutions.

Analysis of Air Samples in ICl

Four samples from the group of air samples collected and supplied by the Sponsor were selected for mercury analysis. The solutions from the plastic collecting tubes were transferred to volumetric flasks and diluted to 100 ml with water. Aliquots of 25 ml were taken from each flask, made alkaline with NaOH, and reduced with hydroxylamine hydrochloride. Each solution was then aerated, and the air stream was directed through the UV absorption cell of the

atomic absorption spectrophotometer. All readings were off scale, indicating an unusually large amount of mercury was present.

Check Analyses Using the Dithizone Method. To verify the unexpected high level of mercury, additional aliquots of 25 ml were analyzed by the dithizone extraction method. The total mercury content of the collecting solutions was found to be in the range of 120-140 micrograms. This level of mercury strongly indicated a severe blank problem attributable to mercury in plastic collection tubes being leached out by the ICl collecting solution. Mercury compounds are used during the formulation of some plastic materials.

Preparation and Analysis of Synthetic Air Samples

The results obtained on the actual air samples suggested that the ICl system be examined anew, beginning with the materials of construction of the collectors.[4] For that reason, a vaporizer air calibration assembly (Figure 1) was employed.[19] The manifold containing the hypodermic needles, the particulate filter, and the charcoal trap of the NASN sampler were retained (Figure 1). However, the glass intake manifold was isolated from the system, the plastic collector tube was converted into a scrubber containing alkaline thiosulfate solution, and a direct connection was made between it and the charcoal trap. The glass impinger with the vaporizer attached was then connected to the thiosulfate scrubber.

To operate, stopcock B-2 was closed, 0.1 ml of a standard mercury solution was added to the vaporizer, and the stopper with stopcock B-1 in closed position was put in place. The vacuum pump was started, and after 5 to 10 seconds stopcock B-2 was opened. Then after a few seconds the upper stopcock B-1 was opened slowly. Air was then passed through the system for the required length of time. A blank run was made at the same time to monitor the laboratory air being

drawn through the system. Air flow calibration runs were made to establish conditions yielding flow rates of approximately 0.2 and 2.0 liters per minute.

A standard solution of dimethyl mercury was prepared by dissolving 84.1 mg dimethyl mercury (equivalent to 73.2 mg Hg) in 100 ml of toluene, or 732 micrograms Hg per ml. Successive 1:10 dilutions of this solution provided standard solutions A, B, and C containing 0.732, 7.32, and 73.2 micrograms Hg per ml, respectively.

A microsyringe was used to measure 0.1 ml of solution A and place it in the vaporizer. The vacuum pump was started, the stopcocks on the vaporizer were opened, and the run continued for 1.5 hours. At a flow rate of 0.2 l/min, this equals 73.2 ng Hg/0.018 m^3, or 4070 ng/m^3 average. This procedure was repeated with 0.1 ml of solution B (average Hg concentration equals 40.7 $\mu g/m^3$) and again with solution C (average Hg concentration equals 407 $\mu g/m^3$), a freshly prepared impinger containing 25 ml of ICl collecting solution being used for each. A 97 percent recovery was obtained by the dithizone-AAS method on the 7.32 µg Hg addition. The lower concentrations of Hg additions were recovered with considerably less efficiency as judged by the atomic absorption results. However, these apparently low recoveries may be due to variable blank, possible spectral interference of the iodine monochloride encountered in the atomic absorption procedure, or adsorption, of Hg on the container walls.

The same volatilization apparatus was used to test the efficiency of the ICl - glass impinger collecting system under conditions of high loading (5-15 micrograms Hg) and high air flow (1.7 l/min).

Three calibration runs were made at the 1.7 l/min air flow rate with 5.32, 10.6, and 14.9 micrograms of mercury as dimethyl mercury in toluene added respectively via the vaporizer. Glass microimpingers containing 25 ml of ICl solution were used for collecting the vapor. Three standards were prepared by adding the same amounts of the standard dimethyl mercury - toluene

solution to 25 ml portions of the ICl solution. The mercury content of the three standards and the three test solutions were determined by a dithizone method. The results are shown in Table 1.

TABLE 1. RECOVERY OF DIMETHYL MERCURY

(Flow rate 1.7 liters per minute)

Sample	Hg Added, micrograms	Hg Found, micrograms	Absolute Recovery, percent	Recovery Based on Standards, percent
Std.$_1$ (a)	5.32	4.7	88	-
Std.$_2$ (a)	10.6	9.9	93	-
Std.$_3$ (a)	14.9	13.2	89	-
Run 1 (b)	5.32	3.6	-	76
Run 2 (b)	10.6	7.2	-	73
Run 3 (b)	14.9	9.6	-	73
		average	90, σ = 3	74, σ = 2 *

(a) Toluene solution of dimethyl mercury added directly to ICl solution.
(b) Toluene solution of dimethyl mercury vaporized and collected in ICl solution.

These data, although not showing as quantitative recovery at the high flow rate as could be desired, nevertheless served to indicate that the system, as used with glass impingers in these experiments, does not give rise to high mercury values. By implication, therefore, it can be postulated that the very high mercury values obtained in the analysis of the ambient air samples were caused by contamination from the reagents or more importantly from the plastic impinger bottles.

By mutual agreement between BCL and the EPA Project Officer it was agreed that further work on Phase III (sample analysis) be suspended indefinitely owing to the high and undoubtedly incorrect mercury values obtained for the few samples analyzed. The available time and funds were directed to additional studies under Phases I and II and, as an extension of the effort, into Phase IV.

* In this report, σ refers to the precision, not accuracy, as calculated by the equation $\sigma = \sqrt{\frac{\Sigma(\bar{R} - R)^2}{n - 1}}$, where $\bar{R}$ and R are the average and individual percent recoveries, respectively.

Double Aeration

Erratic responses often were observed when solutions containing ICl were reduced and aerated directly through the optical cell of the atomic absorption spectrophotometer. This was most apparent when the 3x or 10x expansion scales were used to provide more sensitivity. The source of this erratic behavior was not identified positively, but it appeared to be caused by some interfering substance other than mercury vapor being evolved from the solution. This substance then absorbed ultraviolet energy in the optical cell and caused spurious results. Residual toluene may have been the interfering agent in synthetic samples prepared by vaporizing mercury compounds dissolved in toluene.

An analysis scheme involving double aeration was investigated. By reducing the mercury in the ICl collecting solution, driving the mercury vapor out by aeration, and collecting the mercury vapor in a second absorbing solution which does not contain ICl, it was hoped that the interfering substance would not be absorbed. The second absorbing solution could then be reduced and aerated directly into the optical cell of the AAS.

Five standards were prepared, each containing 25 ml of the ICl collecting solution and 25, 50, 75, 100, and 150 nanograms of mercury as $HgCl_2$, respectively. Each standard was made basic with sodium hydroxide, reduced with hydroxylamine hydrochloride, and aerated for five minutes into a scrubbing bottle containing 50 ml of a 20 percent KBr - 5 percent HCl solution. Each KBr-HCl solution was then made basic with sodium hydroxide, reduced with hydroxylamine hydrochloride, and aerated directly into the optical cell of the AAS operated with the 3x scale expansion. Absorption was measured in chart divisions and plotted against the mercury content of the standards.

Three standards containing 50 ml of the 20 percent KBr - 5 percent HCl solution and 50, 100, and 150 nanograms of mercury were prepared. Each of these standards was made basic with sodium hydroxide, reduced with hydroxylamine hydrochloride, and aerated directly into the measuring system. Absorption was measured in chart divisions and plotted against the mercury content. Results are shown in Figure 5.

The results of this preliminary investigation were quite promising. There appeared to be no serious loss of mercury in the transfer from one collecting system to another and a linear relationship between ultraviolet absorption and mercury content was indicated. However, work on the double aeration technique was suspended so that studies of other aspects of ICl solution collection and analysis could be expedited.

Mercury Vapor Collection

The apparatus shown in Figure 1 was modified by substituting a mercury vapor generator for the vaporizer and was used to test the efficiency of the ICl-glass impinger collecting system under conditions of low loading (20 to 100 nanograms Hg) and high air flow (1.7 l/min).

Three calibration runs were made at the high flow rate of 1.7 l/min with 20, 50, and 100 nanograms of mercury as mercury vapor added by passing the air stream through an aeration cell containing dilute HCl, stannous chloride, and measured amounts of standard mercury $HgCl_2$ solution. The mercury present in the aeration cell was reduced to the elemental form, and mercury vapor was carried by the air stream through a glass impinger containing 25 ml of ICl collecting solution. Mercury in the ICl solution was determined by making the solution basic, reducing with hydroxylamine hydrochloride, and aerating directly into the ultraviolet absorption cell mounted in the optical system of the atomic absorption spectrophotometer. Results are shown in Table 2. The results shown in Table 2,

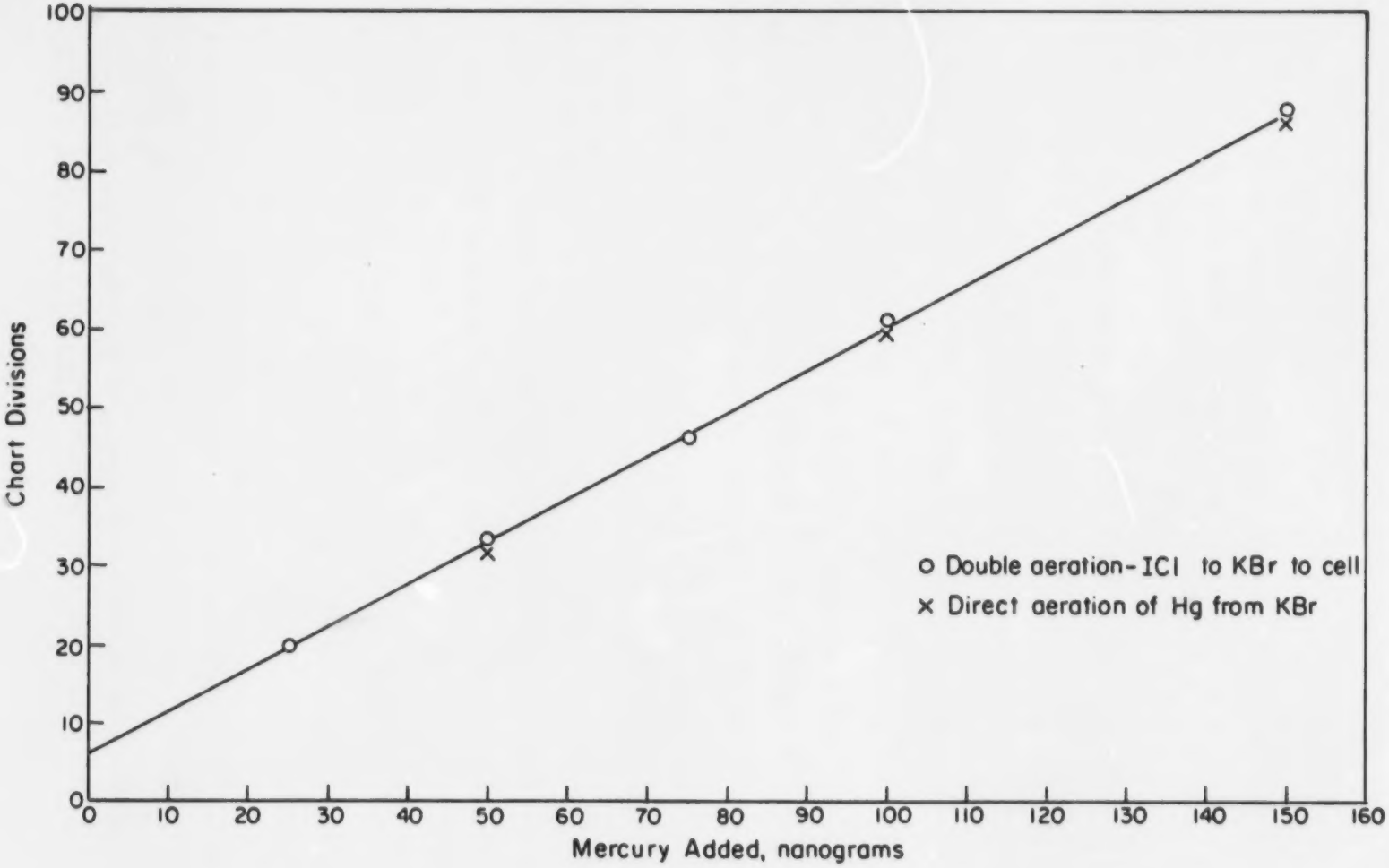

FIGURE 5. OPTICAL ABSORPTION BY MERCURY AT 253.7 nm VERSUS MERCURY CONTENT

TABLE 2. RECOVERY OF MERCURY VAPOR

(Flow rate 1.7 liters per minute)

Hg Added, nanograms	Hg Recovered, nanograms	Recovery, percent
20	17	85
50	48	96
100	98	98
		average 93, σ = 7

namely the recovery of Hg^{o} in ICl under conditions of high air flow rate (1.7 l/min) followed by analysis using aeration directly into the AAS, may be compared with those given in Table 1. The latter data (Table 1) show an overall recovery of about 75 percent and are for the absorption at high flow rates (1.7 l/min) of dimethyl mercury in ICl followed by analysis using the dithizone method. Two variables are involved: the chemical form of mercury presented to the ICl collector and the method of analysis. To check which variable caused the difference in recovery (75 percent for dimethyl mercury - dithizone versus 90^{+} percent for elemental mercury - direct AAS), portions of the experiments were modified and performed as described in the following section.[12]

Flow Rate Experiments

An aqueous stock solution of CH_3HgCl was prepared by dissolving 8.675 mg of the compound in water and diluting to 1 liter.[13] A similar stock solution of $(CH_3)_2Hg$ was prepared by dissolving 6.760 mg of the compound in 25 ml of ethyl alcohol, then diluting to 1 liter with water. Aliquots of these stock solutions were subsequently diluted to give working solutions for use in the experimental runs.

The mercury content of the prepared solutions was checked by adding measured amounts to 25 ml of the iodine monochloride solution, then making the solution basic, reducing with hydroxylamine hydrochloride, and aerating through the AAS. Initial recoveries were quite low, and it was discovered that the organic mercury compounds must react with the iodine monochloride for at least 20 minutes before maximum recoveries were obtained. A procedure including a 30-minute initial reaction period was adopted, and four runs were made on aliquots of each of the stock solutions. Results indicated 85 percent recovery of the $(CH_3)_2Hg$ and 96 percent recovery of the CH_3HgCl. The $(CH_3)_2Hg$ stock solution was considered to contain 5.75 mg mercury per liter, and the CH_3HgCl stock solution was considered to contain 6.65 mg mercury per liter. These values were used to calculate collecting efficiency in the vaporization experiments.

The air calibration assembly shown in Figure 1 was modified to provide for a positive air flow rather than the vacuum system previously used. A diagram of the modified assembly is shown in Figure 2. Air was supplied from a compressed air cylinder, and any mercury vapor which might be present was removed by filtering through a silver wool plug. Flow rates were monitored by a rotameter.

To operate, 25 ml of the ICl collecting solution was placed in the impinger which was then clamped into place. The lower stopcock on the vaporizer was closed, the vaporizer cap was removed, and a measured portion of the standard working solution was transferred to the vaporizer. The vaporizer cap was then quickly replaced. Both vaporizer stopcocks were opened, and the air flow was started and adjusted to the required flow rate. The run was continued for about 45 minutes, after which time the bottom of the vaporizer was heated gently to assure complete vaporization, and the flow continued for an additional 5 minutes. Mercury in the collecting solution was then determined in the usual manner by making it basic with NaOH, reducing it with hydroxylamine hydrochloride, and aerating it through the AAS.

Runs were made with three mercury levels and at two flow rates for each of the compounds tested. Results of these runs are reported in Tables 3 and 4.

TABLE 3. RECOVERY OF VAPORIZED METHYL MERCURIC CHLORIDE

Run	Flow Rate	Hg Added, nanograms	Hg Found, nanograms		Mercury Recovered, percent
1	0.2 liter/min	20	16		80
2	0.2 liter/min	50	37		74
3	0.2 liter/min	50	38		76
4	0.2 liter/min	100	78		78
5	0.2 liter/min	100	78		78
				average	77, σ = 2
6	1.0 liter/min	20	11		55
7	1.0 liter/min	50	38		76
8	1.0 liter/min	100	73		73
				average	68, σ = 11

TABLE 4. RECOVERY OF VAPORIZED DIMETHYL MERCURY

Run	Flow Rate	Hg Added, nanograms	Hg Found, nanograms		Mercury Recovered, percent
1	0.2 liter/min	17	16		94
2	0.2 liter/min	17	12		71
3	0.2 liter/min	43	33		77
4	0.2 liter/min	43	37		86
5	0.2 liter/min	129	117		91
6	0.2 liter/min	129	114		88
				average	85, σ = 9
7	1.0 liter/min	17	11		65
8	1.0 liter/min	17	11		65
9	1.0 liter/min	43	27		63
10	1.0 liter/min	43	29		67
11	1.0 liter/min	129	89		69
12	1.0 liter/min	129	91		71
				average	67, σ = 3

These experiments clearly show that collection efficiency may be function of the flow rate. This dependency may be especially important when the volatilization method is used to introduce the mercury compound into the gas stream, because the volatilization has a tendency to occur over a small time span, not necessarily uniformily throughout the total air flow period.

Furthermore, Tables 3 and 4 show that the flow rate dependency (at least with the unknown variable of volatilization rate) is not the same for different compounds. Methyl mercuric chloride showed no consistent rate dependency, while dimethyl mercury showed better recovery at the lower air flow rate. Thus, on the basis of the data available, it appears that the collection efficiency for mercury also depends to some extent upon the form in which the mercury is present in the air, given a constant set of sampling conditions. Returning briefly to the data presented in Tables 1 and 2, it seems probable that the difference in recovery can be attributed to the difference of chemical form, rather than to the method of analysis. The need for more definitive experiments to test this conclusion are apparent, and such experiments are suggested in the recommendations for Future Work section.

As noted earlier, no further work was performed on the analysis of EPA-collected samples because excessively high values had been obtained for mercury in those few samples analyzed. Instead, at the request of the Project Officer efforts were directed to the evaluation of other systems, as described in the following sections of this report.

Evaluation of a Commercial Mercury Vapor Detection System[7,10,16]

About midway in this program, EPA desired an evaluation of an instrument designed to determine mercury vapor (Hg^{o}) in ambient air. These studies are reported in this section.

Principle of Operation

The subject of this evaluation was an instrument for atmospheric mercury vapor detection purchased by EPA and delivered to Battelle's Columbus Laboratories for evaluation. This instrument consists of two units, a mercury converter and a condensation nuclei monitor. Samples are collected by drawing air through a sampling cartridge containing a plug of silver wire. The cartridge is then placed in the mercury converter and connected to a source of compressed air. The collected mercury is released by heating, and the resulting mercury vapor is irradiated by ultraviolet light forming submicroscopic particles of HgO. These nuclei are carried by the air stream into the condensation nuclei monitor where they are passed through a cloud chamber. Water vapor condenses on the nuclei, and droplets are formed which may be counted by optical and electronic circuits.

Preliminary Evaluation

The instrument as received at Battelle's Columbus Laboratories was first used to measure mercury collected in laboratory air. Consistent duplication of results on samples taken simultaneously could not be achieved; after two weeks, the instrument failed to give a response to any samples introduced into the system.

A representative of the manufacturer was informed of the difficulty, and he came to Battelle to inspect the instrument and to try to resolve the difficulties. He found that the ultraviolet lamp was coated by a thin film. This film was removed, but during the operation the aperture regulating the amount of effective ultraviolet energy in the system was altered slightly. When the background count remained high, he also removed a small humidifying unit from the converter unit, explaining that too much water vapor at this point in the system sometimes led to high counts.

The mercury vapor detection system, altered as explained above, was used for the tests described in this report. The instrument's sensitivity was drastically lower than indicated by the operating manual. Standards were not reproducible consistently, and over a five-day period of testing there were three occasions when the instrument failed to operate.

Evaluation Using Permeation Tubes

An apparatus employing a permeation tube was constructed to supply a constant amount of mercury vapor in a gas stream. A diagram of the apparatus is shown in Figure 3.

The permeation tube was constructed by placing about 10 grams of mercury in silicone rubber tubing (1.25-cm ID, 0.48-cm wall thickness [1/2-inch ID, 3/16-inch wall thickness]) plugged on both ends with Teflon. The length of tubing between the two end plugs was approximately 2.2 cm (7/8-inch).

The permeation tube and a thermometer were placed in the water-jacketed condenser. The circulating water in the condenser jacket was maintained at 31° C. Nitrogen gas was passed through the constant temperature bath and then through the condenser at a rate of 220 ml/min.

After allowing the system to equilibrate for 24 hours, it was calibrated by passing the nitrogen gas into impingers containing 25 ml of iodine monochloride solution, timing each collection with a stopwatch. The collected mercury in each impinger was then determined by making the solution basic with NaOH, reducing with hydroxylamine hydrochloride, and aerating through the ultraviolet absorption system. Samples were collected for 5, 7, and 10 minutes. An average of three runs indicated a mercury vapor flow of 15 ± 1 nanograms per minute ($\approx$ 70 $\mu g/m^3$) from the permeation tube assembly.

Four silver-plug sampling cartridges, designated 103, 106, 110, and 114, were selected for the initial phase of the study. Samples of mercury were collected by connecting a cartridge directly to the gas stream passing through the permeation

tube assembly. Each sampling period was timed with a stopwatch. Since the working range of the instrument was expected to be approximately 0.2 to 1.0 nanograms of mercury, the first samples were taken for intervals of 5 seconds to give approximately 1.3 nanograms of mercury. These samples gave no response on the instrument. Subsequent samples collected for 10, 15, 20, 30, and 60 seconds, giving a range of approximately 2.5 to 15 nanograms of mercury, also failed to produce a response on the instrument. Sampling times were increased; and, finally, two samples collected for 5 minutes, representing approximately 75 nanograms of mercury, produced responses above the background count. ("Normal" ambient air contains perhaps 1/100th of that amount; the exact figure is still uncertain.)

Cartridges 110 and 114 were selected for subsequent tests and the instrument was operated for a week. Results of the test runs are reported in Table 5. It should be noted that the response of the instrument, registered as the number of nuclei per milliliter, is a logarithmic function of mercury concentration. Background readings were between 800 and 1400 counts.

During the first three days of evaluation samples containing the same amount of mercury (300 nanograms) were prepared and measured on the instrument. Results varied widely, and on two occasions the program was interrupted by failure of the instrument to give any response. In each instance the instrument was turned off; when reactivated later, it registered counts once more.

On the fourth day of testing, samples were collected for four different time intervals, and an attempt was made to draw a calibration curve. As shown in Figure 6 the results obtained with cartridge 110 produce a smooth calibration curve. However, cartridge 114 produced scattered data, especially at the 225 nanograms level, and a calibration curve could not be drawn.

TABLE 5. RESULTS OF EVALUATION

Date	Cartridge Number	Sampling Time, minutes	Mercury Added, nanograms	Count
September 20, 1971	110	20	300	7,500
	110	20	300	16,500
	110	20	300	9,000
September 21, 1971	110	20	300	68,000
	110	20	300	2,600
	110	20	300	2,400
	110	20	300	No response
September 22, 1971	110	20	300	400,000
	114	20	300	25,500
	110	20	300	180,000
	114	20	300	15,500
	110	20	300	145,000
	114	20	300	No response
	110	20	300	215,000
	114	20	300	40,000
	110	20	300	275,000
	114	28	420	150,000
	110	22	330	400,000
September 23, 1971	114	23.5	352	110,000
	110	20	300	220,000
	114	15	225	10,000
	110	15	225	96,000
	114	10	150	4,600
	110	10	150	29,000
	110	5	75	3,900
	114	5	75	1,100
	114	15	225	40,000
	114	15	225	120,000
September 24, 1971	110	20	300	1,300
	114	20	300	No response

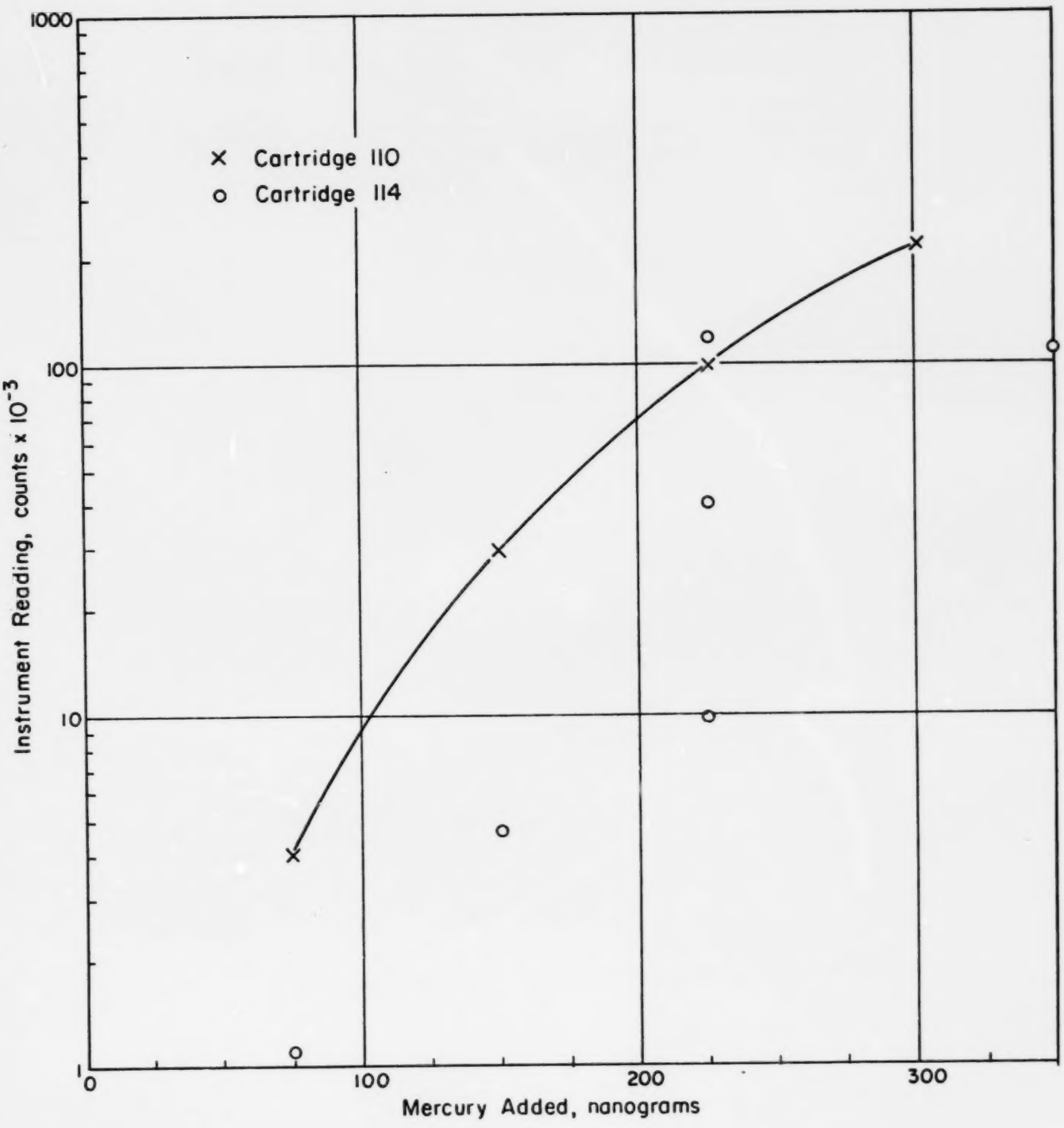

FIGURE 6. RESULTS OF CALIBRATION RUNS

On the following day two samples were run, each containing 300 nanograms of mercury. The registered count on the first sample was barely above background, and no counts were registered with the second sample. At this point, evaluation was halted.

The mercury vapor detection system was returned to the manufacturer on October 19, 1971, at its request.

Evaluation of a Mercury Collection Instrument

This work, in which Battelle participated only to the extent of supplying known samples, is reported here to follow up the mention of this instrument in a monthly letter report[12].

Nine gold screens, supplied by the manufacturer, were loaded with known amounts of mercury using the permeation tube assembly described above (Figure 3). These screens were loaded using a battery-powered air suction pump (sniffer). Via EPA, these screens were returned to the manufacturer and analyzed by using their instrument. The manufacturer's results via EPA are given in Table 6.

TABLE 6. RESULTS OF EVALUATION RUNS[a]

Hg Added, nanograms	Hg Found, nanograms		Recovery, percent
25	23.4		94
25	22.5		90
25	23.6		94
		average	93
50	52		104
50	50		100
50	49.5		99
		average	101
100	104		104
100	115		115
100	105		105
		average	108
	overall	average	101

(a) Data via Dr. R. J. Thompson, EPA.

PHASE IV

Introduction

This phase was initiated late in the program period as part of a joint concentrated effort with EPA to evaluate a system designed by EPA as an alternative to the ICl technique for collecting mercury from ambient air. As discussed previously, ICl does collect total mercury but presents analytical difficulties; other collection devices are not effective for all forms of mercury. The operating principle of the method is described in the next section.

Principle of Operation

Mercury is collected (amalgamated) on many metals. For this amalgamation to occur, the collecting metal must be clean, i.e., present a surface with which the mercury can alloy. The mercury itself must be in an elemental form. Thus, compounds such as $(CH_3)_2Hg$ are not collected on metals which form an amalgam with elemental mercury.

The present concept utilizes a pyrolysis furnace in which mercury compounds are converted into Hg° by virtue of the thermal instability of almost

all mercury compounds. (HgO, for example, is decomposed as $HgO \longrightarrow Hg + [O]$; at 500°C the partial pressure of oxygen over HgO is about 980 mm.) The products of pyrolysis, including Hg^{o} vapor, are passed through a collector maintained at a temperature near ambient. The collector is a Pyrex, or preferably Vycor, tube packed with silver wool with which the mercury amalgamates. The experiments designed to evaluate this concept for collection efficiency and for interferences are described in the next sections.

EXPERIMENTAL WORK

Construction of Equipment[17]

Twelve collector tubes were constructed of 7-mm Pyrex tubing with 12/5 male and female ball joints on each end, respectively. These tubes duplicate, as nearly as possible, the collector tube used by EPA in concurrent experiments on this concept. Each was wound with 100 cm (3 feet) of 22-gage Chromel A wire and loaded with 1 gram of silver wool cleaned at 700° C before use. A drawing of the collector tube is shown in Figure 7.

Two catalyst pyrolysis tubes were constructed of 7-mm Vycor tubing with 12/5 male and female ball joints on each end, respectively. These tubes are 20 cm (8 inches) in length with identations at 5 cm (2 inches) and 12.5 cm (5 inches) from the inlet end to aid in holding the catalyst material and provide a 8 cm (3 inch) heating zone. The tubes were packed alternately with CuO, silver wool, silver tungstate/MgO, and CuO. A small plug of quartz wool was added at each end of the catalyst material to hold it in place. The heating zone was wrapped with 150 cm (5 feet) of 22-gage Chromel A wire. A thermocouple was placed next to the tube in the middle of the heating zone and the heating zone was covered with asbestos. A drawing of the catalyst tube is shown in Figure 8.

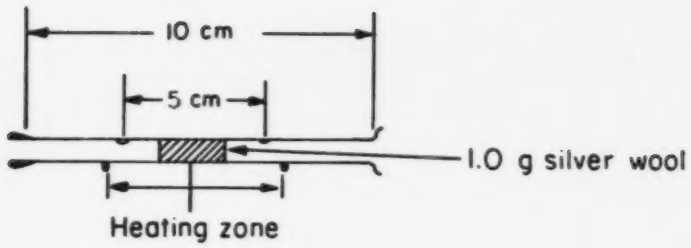

FIGURE 7. COLLECTOR

Tube - 6-mm ID Pyrex with 12/5 ball joints.

Heating zone wrapped with 100 cm of 22 gage Chromel A wire.

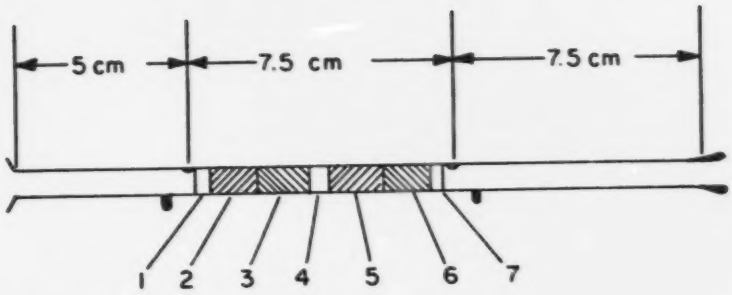

FIGURE 8. PYROLYSIS TUBE

Tube - 7-mm ID Vycor with 12/5 ball joints.

Tube Packing

(1) Quartz wool
(2) Copper oxide
(3) Silver tungstate/MgO
(4) 0.5 g silver wool
(5) Silver tungstate/MgO
(6) Copper oxide
(7) Quartz wool

Heating zone wrapped with 150 cm of 22-gage Chromel A wire and covered with asbestos.

Calibration and Efficiency Experiments

Calibration by Aeration

The collector tubes were conditioned by passing a stream of nitrogen through them at a rate of 300 ml per minute and heating them electrically at about 300° C for 30 seconds. They were then cooled and capped.

The collection and detection systems were standardized by the aeration technique. Mercury was vaporized from mercuric chloride solutions by bubbling air through the solution at a rate of 300 ml per minute, after reduction of Hg^{2+} to Hg° by stannous chloride. This air flow, containing the mercury vapor, was passed through the collector tubes for 2 minutes.

The collector tubes, containing the absorbed mercury, were then placed in a 300 ml/minute nitrogen stream leading to the 15-cm (6-inch) absorption tube mounted on the Perkin-Elmer Model 303 atomic absorption spectrophotometer. This absorption tube was centered on the isolated 253.7-nm mercury line generated by a hollow cathode mercury tube. The mercury contained in the collector tube was released by heating to about 300° C for 30 seconds. The optical absorbance of the released mercury vapor was measured by the spectrophotometer and recorded on a strip chart. Results of the standardization runs are shown in Table 7. Replication of results was very good. At the 20-nanogram mercury level, seven measurements showed an average deviation of 5.0 percent. The 13 measurements made at the 100-nanogram level had an average deviation of 2.6 percent.

Averages of all peak height readings taken at the five concentrations of mercury (20, 50, 100, 150, 200 nanograms) were converted to absorption units to provide a more linear curve and were used to construct the standard curve shown in Figure 9. This curve was used to check recoveries of mercury in the experiments that follow.

TABLE 7. STANDARDIZATION OF COLLECTORS BY AERATION

Collector No.	Mercury Added, Nanograms	Peak Height, Chart Division	Absorption Value
Blank	0.0	none	0.0000
1	20.0	14.0	0.0655
1	20.0	13.0	0.0605
1	50.0	28.0	0.1427
1	50.0	28.5	0.1457
1	100.0	47.5	0.2798
1	100.0	48.0	0.2840
1	100.0	48.5	0.2882
1	150.0	60.0	0.3979
1	150.0	59.0	0.3872
1	200.0	68.5	0.5017
1	200.0	67.5	0.4881
Blank	0.0	1.0	0.0044
2	20.0	12.5	0.0580
2	50.0	27.5	0.1397
2	150.0	61.5	0.4145
3	20.0	12.5	0.0580
3	100.0	51.5	0.3143
3	100.0	51.5	0.3143
3	200.0	68.5	0.5017
4	20.0	13.5	0.0605
4	100.0	48.0	0.2840
5	20.0	12.0	0.0555
5	100.0	50.0	0.3010
6	20.0	12.0	0.0555
6	100.0	48.0	0.2840
7	20.0	12.5	0.0580
7	100.0	47.0	0.2757
8	100.0	4910	0.2924
9	100.0	48.5	0.2882
10	100.0	51.0	0.3098
11	100.0	50.0	0.3010

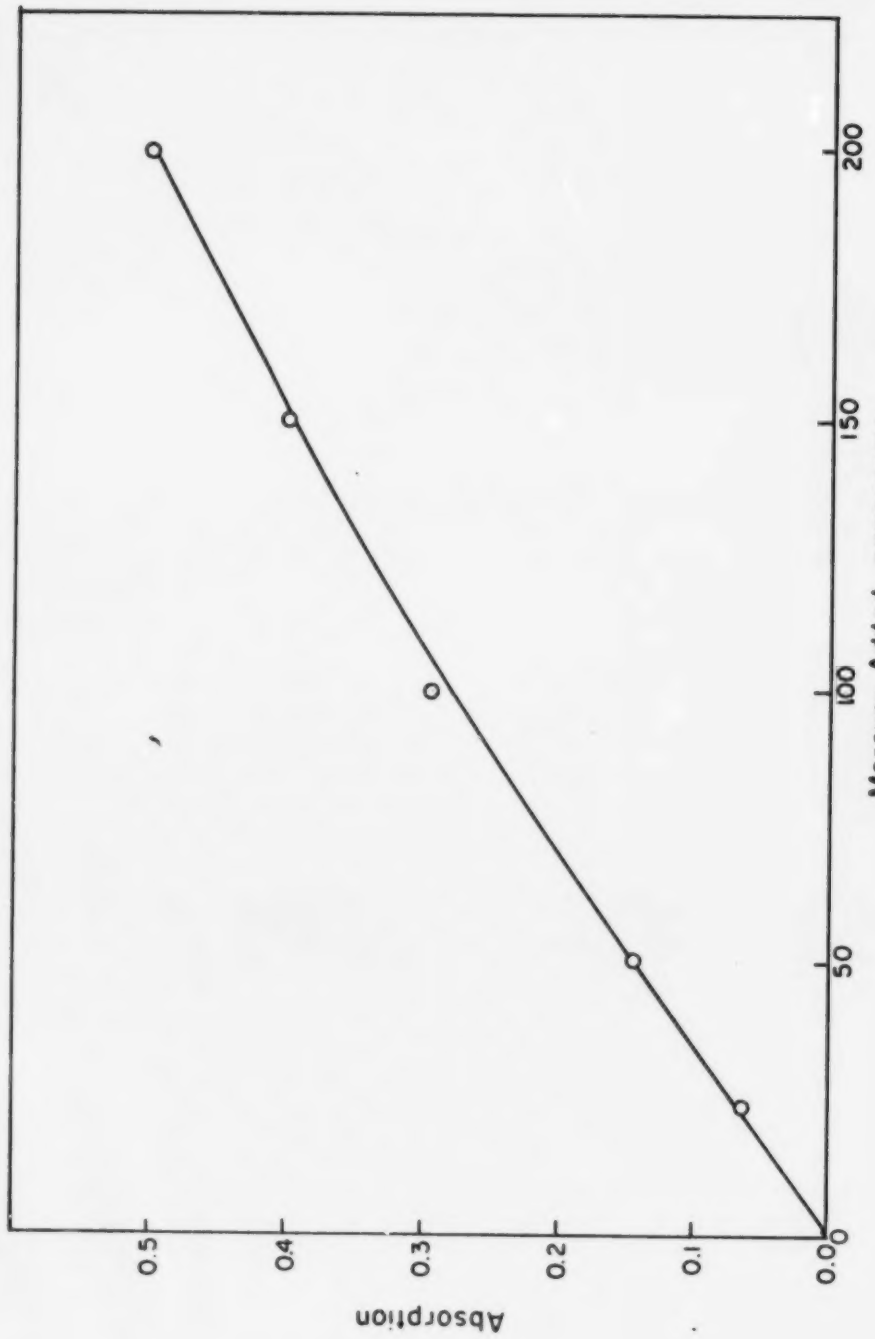

FIGURE 9. CALIBRATION CURVE FOR SILVER COLLECTORS

Direct Loading of Collectors From Permeation Tube Assembly

A mercury vapor permeation tube assembly was constructed as shown in Figure 4. The permeation tube contained about 10 grams of mercury in silicone rubber tubing (1.25-cm ID, 0.48-cm wall thickness [1/2-inch ID, 3/16-inch wall thickness]) plugged on both ends with Teflon. The length of tubing between the two end plugs was approximately 2.2 cm (7/8 inch). For this work nitrogen gas was passed through the system at 100 ml per minute, and the circulating water in the condenser jacket was maintained at 26° C. The calculated permeation rate at this temperature is 10.7 nanograms of Hg per minute, based on previous calibrations at 23.5° C and 31° C. (This is equivalent to 107 $\mu g/m^3$. or about 80 ppb Hg.)

After allowing the system to equilibrate, a series of runs was made in which the collector tubes were connected directly to the outlet and loaded by the mercury in the gas stream. Each run was carefully timed with a stopwatch. The mercury retained by each collector was then released by heating and measured as described in the preceding section. Results of these runs are shown in Table 8. Replication again was very good. Peak height readings on the 3, 6, and 15-minute runs (32.1, 64.2, and 160.5 ng Hg, respectively) show an average deviation of 4.4, 3.0, and 1.8 percent, respectively. The accuracy of the system is indicated by the 105, 100, and 98 percent average recovery of added mercury on the 3, 6, and 15 minute runs, respectively.

Mercury Vapor Loading Through the Catalyst Furnace

The first two catalytic pyrolysis furnaces cracked when brought up to temperature. Although the cause of these mishaps is not certain, the catalytic material probably had been packed too tightly. A third furnace was constructed as described above (Figure 2), baked out slowly, and finally brought up to 600°C and conditioned at this temperature for 3 hours. The temperature was monitored with

TABLE 8. RESULTS OF DIRECT PERMEATION TUBE LOADING

Collector Number	Time of Run, minutes	Peak Height, chart division	Absorption Value	Mercury Added, nanograms	Mercury Found, nanograms
1	3	20.5	0.0996	32.1	31
2	3	21.5	0.1051	32.1	33
3	3	22.5	0.1107	32.1	35
5	3	22.0	0.1079	32.1	35
6	3	20.5	0.0996	32.1	31
7	3	21.0	0.1024	32.1	32
8	3	20.5	0.0996	32.1	31
9	3	23.0	0.1135	32.1	36
10	3	23.0	0.1135	32.1	36
11	3	23.0	0.1135	32.1	36
1	6	35.0	0.1871	64.2	63
2	6	36.5	0.1972	64.2	66
4	6	37.0	0.2007	64.2	66
6	6	37.0	0.2007	64.2	66
7	6	34.0	0.1805	64.2	60
8	6	34.5	0.1838	64.2	61
10	6	35.5	0.1904	64.2	64
11	6	37.0	0.2007	64.2	66
1	15	61.5	0.4145	160.5	157
3	15	61.5	0.4145	160.5	157
5	15	63.0	0.4318	160.5	165
7	15	60.0	0.3979	160.5	150
9	15	59.5	0.3979	160.5	150
11	15	63.0	0.4318	160.5	165

a thermocouple-potentiometer and controlled with a Variac. The furnace was the attached to the exit end of the permeation tube assembly, and a collector tube (a separate one for each test run) was attached to the outlet of the catalytic tube.

The first three runs showed good recovery of added elemental mercury, but the recoveries on the next three runs dropped considerably. A close examination of the catalyst assembly revealed the presence of fine dust particles adhering to the inside walls of the outlet and of the tube. This portion of the tube was cleaned carefully and heated briefly with a flame to drive off any mercury which might be present. The system was then reassembled, and the runs were resumed with the results reported in Table 9 . The average recoveries were 90 percent for the 3-minute runs, 98 percent for the 6 minute runs, and 95 percent for the 15-minute runs.

Interference Evaluation

Studies of Possible Interference From SO_2

A new catalyst unit was constructed, and all catalyst material was loaded from the entrance end. This was done to reduce the risk of contaminating the exit end of the tube with fine powders which might act as mercury vapor collectors. A Wheelco furnace controller was substituted for the Variac to control the temperature of the catalyst zone more closely.

The catalyst unit was attached to the exit of the mercury permeation tube assembly as before. An SO_2 permeation tube with a calibrated weight loss of 0.37 microgram per minute was placed, together with the mercury permeation tube, in the water jacketed section of the mercury vapor permeation tube assembly (Figure 4). This provided a gas stream with an SO_2 concentration nearly 35 times that of the mercury vapor concentration. Runs of 3, 6, and 15 minutes were made. The results obtained are shown in Table 10. The average recoveries of 102, 96, and 98 percent

TABLE 9. RESULTS OF MERCURY VAPOR LOADING THROUGH THE CATALYST FURNACE

Collector Number	Time of Run, minutes	Peak Height, chart division	Absorption Value	Mercury Added, nanograms	Mercury Found, nanograms
6	6	35.0	0.1871	64.2	62
7	6	34.0	0.1805	64.2	60
9	6	33.5	0.1772	64.2	58
10	6	35.0	0.1871	64.2	62
11	6	35.5	0.1904	64.2	63
1	6	37.0	0.2007	64.2	66
2	6	36.0	0.1938	64.2	64
3	6	37.0	0.2007	64.2	66
4	3	20.5	0.0996	32.1	32
5	3	18.0	0.0862	32.1	27
7	3	19.5	0.0942	32.1	30
1	15	61.0	0.4089	160.5	155
3	15	62.0	0.4200	160.5	160
5	15	59.5	0.3925	160.5	147
9	15	59.0	0.3872	160.5	145

TABLE 10. MERCURY RECOVERY FROM GAS STREAM CONTAINING SO_2
(SO_2 Rate = 0.37 Microgram Per Minute)

Collector Number	Time of Run, minutes	Peak Height, chart division	Absorption Value	Mercury Added, nanograms	Mercury Found, nanograms
1	3	20.5	0.0996	32.1	32
2	3	22.5	0.1107	32.1	35
3	3	21.5	0.1051	32.1	33
4	3	20.5	0.0996	32.1	32
5	3	20.0	0.0969	32.1	31
6	3	20.0	0.0969	32.1	31
9	3	20.5	0.0996	32.1	32
10	3	23.0	0.1135	32.1	36
11	3	20.0	0.0969	32.1	31
3	6	35.5	0.1904	64.2	63
4	6	35.0	0.1871	64.2	62
5	6	34.8	0.1860	64.2	61
6	6	34.0	0.1805	64.2	60
9	6	35.5	0.1904	64.2	63
10	15	63.0	0.4318	160.5	165
11	15	62.5	0.4260	160.5	163
1	15	60.0	0.3980	160.5	150
2	15	60.0	0.3980	160.5	150

of the added mercury on the 3, 6, and 15 minute runs indicate that SO_2 at a concentration of 3.7 micrograms per liter, much higher than would be expected in ambient air sampling, has little or no effect on the efficiency of the system.

Alteration of Mercury Permeation Tube Assembly. The mercury vapor permeation tube assembly described above[17] was modified by adding a second temperature controlled chamber and an air stream splitter[18]. These alterations were made in order to add small measured amounts of SO_2, H_2S, and NO_2, respectively, to the air stream containing mercury vapor. The modified assembly is shown in Figure 10.

Compressed air, controlled with a needle valve and monitored by Rotameter A, flows through the chamber containing the SO_2, H_2S, or NO_2 permeation tube. A pump draws air, controlled with a needle valve and monitored by Rotameter B, through the chamber containing the mercury permeation tube. By varying the flow of compressed air through Rotameter A and bleeding off measured amounts of this flow through Rotameter C, small measured amounts of SO_2, H_2S, or NO_2 may be introduced into the air stream carrying mercury vapor.

Standard Curve Based on Peak Area. During this phase of the experimental program it became evident that peak areas rather than peak heights provided more accurate measurements of mercury by atomic absorption. Consequently, all the calibration data reported in Table 7 were recalculated as peak areas and were used to construct the calibration curve shown in Figure 11. Ideally, of course, the integrated absorbance (a function of peak area) would be plotted; instead, peak areas were plotted for expediency. As noted in the text accompanying the tables that follow, some recovery data were calculated using the peak height (absorbance) calibration plot (Figure 9), and some using the peak area calibration plot (Figure 11). The latter, as mentioned above, are believed to be more valid because some peak broadening was observed, especially upon the addition of "interfering"

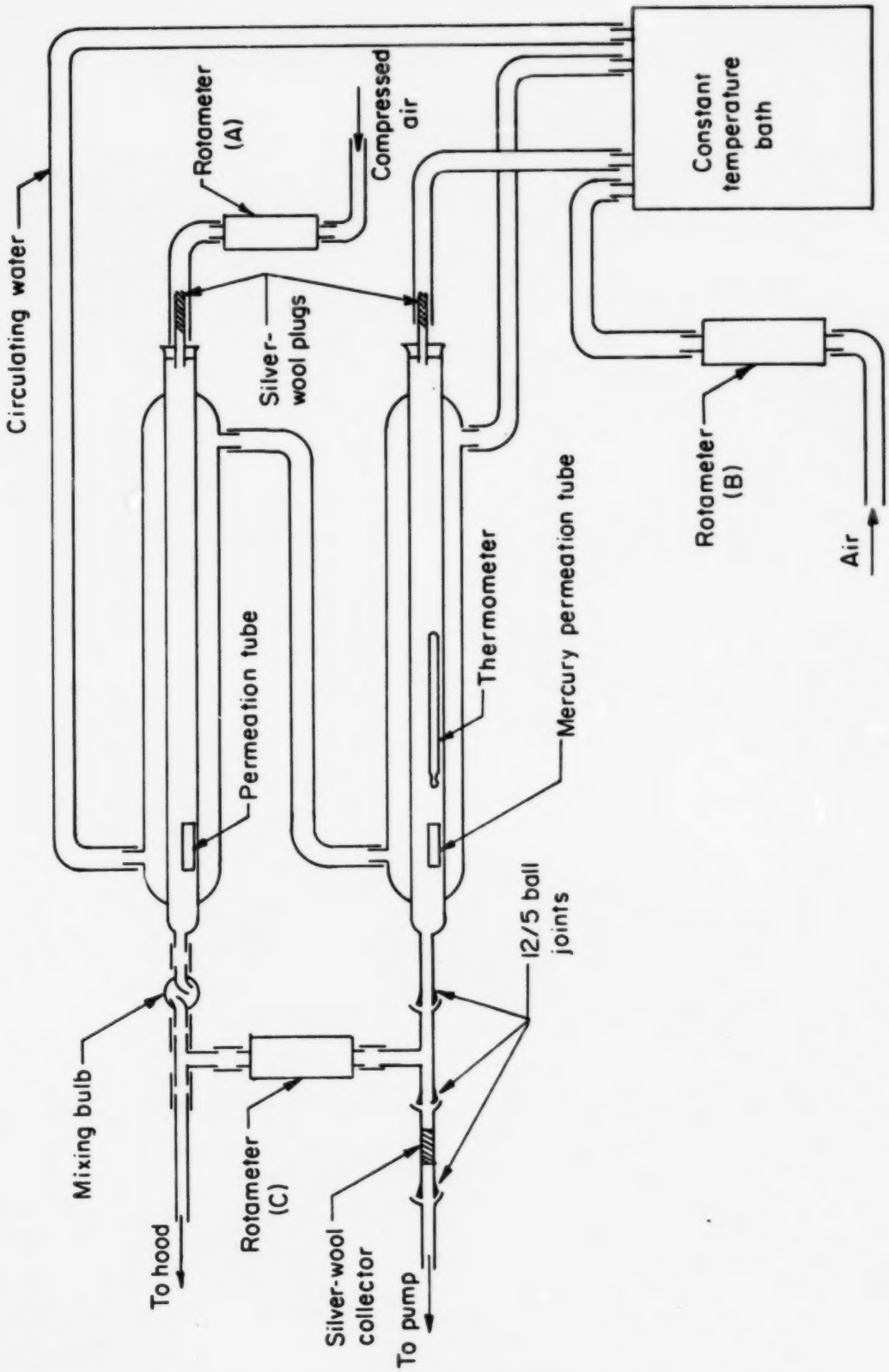

FIGURE 10. MODIFIED PERMEATION TUBE ASSEMBLY

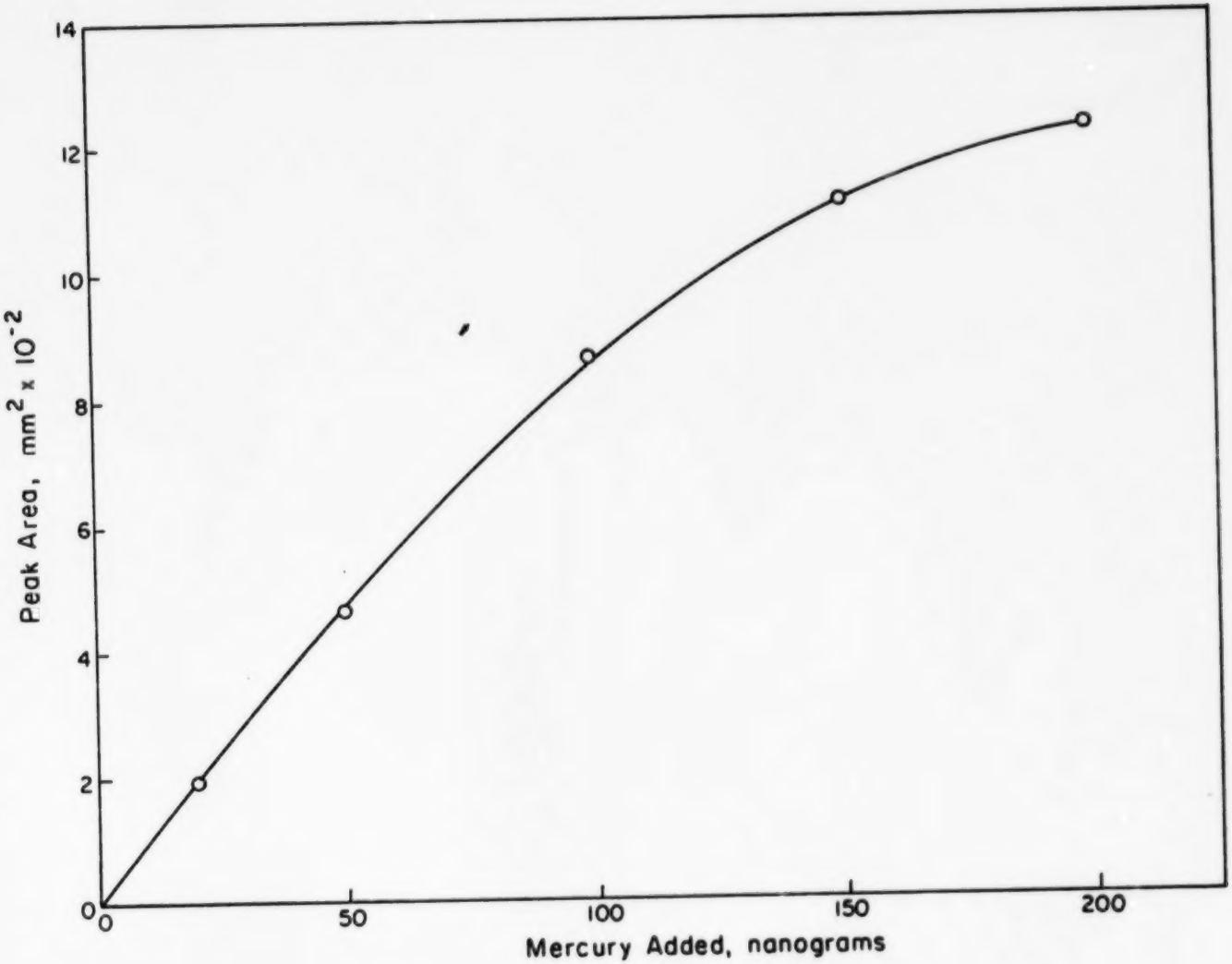

FIGURE 11. CALIBRATION CURVE FOR SILVER COLLECTORS, BASED ON PEAK AREAS

gases - SO_2, H_2S, and NO_2 - to the gas stream. Although some of the broadening of peaks observed during these experiments may have been caused by the gas additives, it is also possible that small changes in the geometry and/or the heating efficiency of the collector tubes, caused by repeated heating and cooling, contributed to this altered response.

Experiments Using Redesigned Equipment. An SO_2 permeation tube was placed in the permeation tube assembly (Figure 10), and mercury collections were made at SO_2 levels of 180, 120, and 37 $\mu g/m^3$. Results obtained for the three sets of runs calculated from the peak area calibration curve (Figure 11), are reported in Table 11. A slight negative bias is indicated with an SO_2 concentration of 180 $\mu g/m^3$. Concentrations of 120 and 37 μg SO_2/m^3 appear to have no effect on the collection and measurement of mercury vapor.

Studies of Possible Interference From H_2S

The equipment setup for the first two experiments was as shown in Figure , with one of two H_2S permeation tubes and the mercury tube together in the permeation tube section [17]. Two runs were made, one with an H_2S permeation tube with a permeation rate of 1.31 micrograms per minute and the other with an H_2S permeation tube with a permeation rate of 1.60 micrograms per minute. This provided gas streams containing 13.1 and 16.0 micrograms of H_2S per liter, a concentration about two orders of magnitude higher than would be expected in ambient air. Results of the two series of runs are shown in Table 12. These data were obtained from the absorbance calibration curve, Figure 9. Even at this high concentration of H_2S the recovery of mercury is about 90 percent.

Experiments Using Redesigned Equipment. An H_2S permeation tube was placed in the temperature controlled chamber shown in Figure 10 [18]. Air flows were adjusted to provide an H_2S concentration of 650 $\mu g/m^3$ and a mercury concentration of 107 $\mu g/m^3$, and a series of runs was made. In subsequent runs the H_2S

TABLE 11. RECOVERY OF MERCURY FROM GAS STREAM CONTAINING SO_2

Run No. 1

SO_2 Concentration = 180 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
1	2.31	32	24	
2	2.84	32	30	
3	2.74	32	29	
4	2.74	32	29	
5	2.96	32	31	
6	3.20	32	34	
9	2.79	32	30	
10	2.84	32	30	
11	5.61	75	61	
1	3.26	43	34	
2	3.79	43	40	
3	2.79	32	30	
6	2.93	32	31	90.0

Run No. 2

SO_2 Concentration = 120 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery Percent
9	3.06	32	32	
10	3.42	32	36	
11	4.18	43	45	
1	2.83	32	30	
11	3.14	32	33	
2	1.16	11	12	
1	3.32	32	35	
11	3.00	32	32	
1	2.71	32	29	102.0

TABLE 11. (Continued)

Run No. 3

SO_2 Concentration = 37 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
2	5.26	59	57	
3	3.62	32	38	
4	3.22	32	34	
5	3.55	32	37	
6	3.47	32	37	
9	3.47	64	67	
10	6.10	64	68	
11	8.83	107	106	
11	3.07	32	32	
10	3.49	32	37	
9	3.21	32	34	
6	3.17	32	33	
5	5.96	64	64	
4	5.98	64	64	100.0

TABLE 12. RECOVERY OF MERCURY FROM GAS STREAM CONTAINING H_2S

Run No. 1

H_2S Concentration = 13.1 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Time of Run, Minutes	Peak Height, Chart Divisions	Absorption Value	Hg Added, Nanograms	Hg Found, Nanograms
1	6	31.5	0.1643	64.2	54
2	6	33.0	0.1739	64.2	57
3	6	35.0	0.1871	64.2	62
4	6	31.5	0.1643	64.2	54
1	6	30.5	0.1580	64.2	52
2	6	32.5	0.1707	64.2	56
4	6	32.5	0.1707	64.2	56
5	6	31.0	0.1612	64.2	52
1	3	19.5	0.0942	32.1	30
2	3	19.0	0.0915	32.1	29
4	3	18.5	0.0888	32.1	29
5	3	18.5	0.0888	32.1	29
6	15	58.5	0.3820	160.5	142
9	15	58.0	0.3768	160.5	140
10	15	58.5	0.3820	160.5	142

Run No. 2

H_2S Concentration = 16 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Time of Run, Minutes	Peak Height, Chart Divisions	Absorption Value	Hg Added, Nanograms	Hg Found, Nanograms
1	3	20.5	0.0996	32.1	31
3	3	20.5	0.1221	32.1	31
4	3	17.5	0.0835	32.1	26
5	3	19.0	0.0915	32.1	29
6	3	18.0	0.0862	32.1	27
10	6	34.0	0.1805	64.2	59
11	6	32.5	0.1707	64.2	56
1	6	31.5	0.1643	64.2	54
2	6	32.0	0.1675	64.2	55
3	6	36.5	0.1972	64.2	65
4	15	61.5	0.4145	160.5	157
5	15	57.0	0.3665	160.5	135
9	15	57.5	0.3716	160.5	138
10	15	59.0	0.3872	160.5	143

concentration was adjusted to 130, 43, and 17 $\mu g/m^3$ for each run, respectively. Results obtained from the four runs are report in Table 13 and are calculated from the peak area calibration curve, Figure11. A slight positive bias is indicated at H_2S concentrations of 650 and 130 $\mu g/m^3$. However, H_2S concentrations of 43 and 17 $\mu g/m^3$ seem to have no effect on the collection and measurement of mercury vapor.

Studies of Possible Interference From NO_2

An NO_2 permeation tube was placed in the proper controlled temperature chamber (Figure 10), and sets of collection runs were made at NO_2 concentrations of 100, 50, and 25 $\mu g/m^3$. Results of the three sets of runs are reported in Table 14 and are calculated from the peak area calibration curve, Figure 11. No interference was noted in the collection and measurement of mercury vapor at any of these NO_2 concentrations.

Mercury Collection From Dimethyl Mercury Vapor

A standard stock solution of dimethyl mercury was prepared by dissolving 114 mg of $(CH_3)_2Hg$ in 500 ml of ethanol to give a solution containing 198.3 µg Hg per ml. A standard working solution was prepared by diluting 1.0 ml of the stock solution to 100 ml with ethanol, giving a solution containing 1.983 µg Hg per ml.

Four runs were made using the vaporizer assembly shown in Figure 12. In each run 50 microliters of the working solution, containing 99.2 nanograms of mercury, were introduced into the vaporizer. The flow rate was controlled at 100 ml per minute and continued for 30 minutes. Results of the four runs are reported in Table 15. No indication of mercury collection was noted.

TABLE 13. RECOVERY OF MERCURY FROM GAS STREAM CONTAINING H_2S

Run No. 1

H_2S Concentration = 650 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
1	3.95	43	42	
2	3.22	32	34	
4	3.58	32	38	
5	3.60	32	38	
9	3.63	32	38	
10	3.43	32	36	
11	3.29	32	35	111.0

Run No. 2

H_2S Concentration = 130 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
1	3.75	32	40	
2	3.09	32	33	
3	3.46	32	36	
4	3.84	32	40	
5	3.37	32	36	
6	3.19	32	34	
9	3.35	32	35	
10	3.51	32	37	
11	6.05	64	67	
1	11.79	161	169	110.0

Run No. 3

H_2S Concentration = 43 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
1	2.89	32	31	
2	2.98	32	32	
3	3.59	32	38	
4	3.03	32	32	
5	3.16	32	34	
6	5.52	64	60	
9	5.82	64	64	
10	5.78	64	64	
11	11.47	161	161	101.00

TABLE 13. (Continued)

Run No. 4

H_2S Concentration = 17 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
3	5.76	64	63	
4	4.03	43	43	
5	3.00	32	32	
6	8.64	107	104	98.8

TABLE 14. RECOVERY OF MERCURY FROM GAS STREAM CONTAINING NO_2

Run No. 1

NO_2 Concentration = 100 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
1	2.79	32	30	
2	3.27	32	34	
3	3.83	32	40	
4	3.51	32	37	
5	3.05	32	32	
6	3.33	32	35	
9	9.61	107	120	
10	4.20	43	45	
11	2.87	32	30	
10	3.01	32	32	
9	3.05	32	32	
6	5.83	64	64	
6	5.73	64	63	
5	5.93	64	65	105.0

Run No. 2

NO_2 Concentration = 50 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found Nanograms	Average Recovery, Percent
11	3.52	32	37	
10	3.23	32	34	
9	4.19	43	45	
6	11.53	161	162	
4	3.81	32	40	
3	3.82	32	40	
2	6.54	64	73	
1	8.32	118	99	
11	5.91	64	65	103.0

TABLE 14. (Continued)

Run No. 3

NO_2 Concentration = 25 $\mu g/m^3$

Hg Concentration = 107 $\mu g/m^3$

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
6	3.24	32	34	
5	3.50	32	37	
4	3.19	32	34	
3	3.25	32	34	
1	5.33	64	58	
11	6.02	64	66	
10	6.32	64	70	104.0

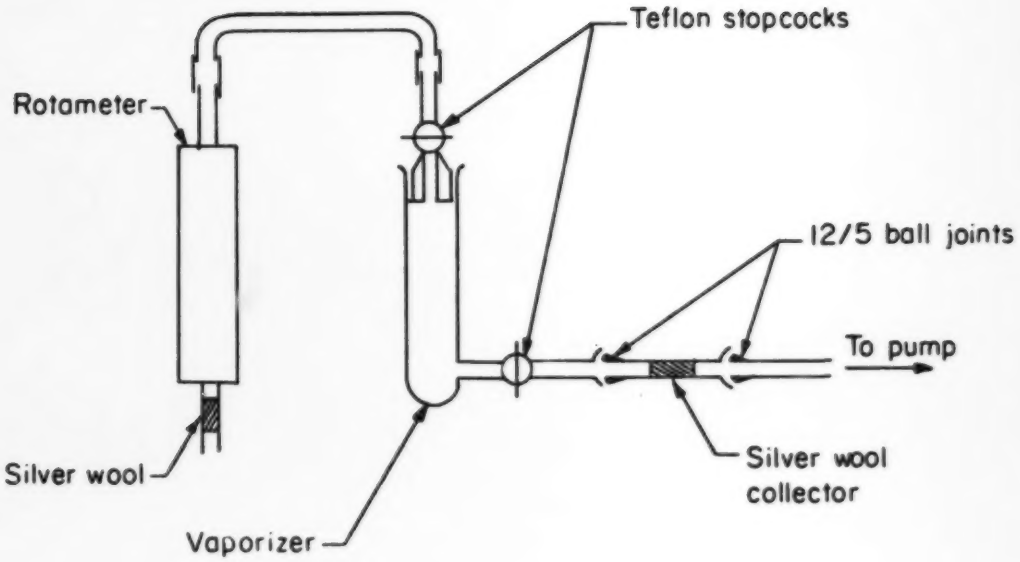

FIGURE 12. VAPORIZER ASSEMBLY

TABLE 15. MERCURY COLLECTION FROM DIMETHYL MERCURY VAPOR

(Silver Wool Collectors Without Pyrolyzer)

Collector	Time of Run, Minutes	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
1	15	99	None	
2	15	99	None	
3	15	99	None	
4	15	99	None	0.0

Collection of Mercury From $HgCl_2$ Particulate Using Pyrolyzer[19]

A stock solution of mercuric chloride was prepared by dissolving 135.4 mg of $HgCl_2$ in 500 ml of ethyl alcohol, giving a concentration of 200 micrograms of Hg per ml. A working solution containing 2 micrograms of Hg per ml was prepared by diluting 1 ml of the stock solution with ethyl alcohol to a volume of 100 ml.

An empty Pyrex collector tube was modified into a vaporizing chamber by heating and blowing out a small buldge in the tubing wall to form a small well to hold the standard $HgCl_2$ solution. A thermocouple was taped to the wall, and the whole tube was wrapped with heating tape and was placed at the entrance end of the pyrolyzer unit. A silver wool collector was attached to the exit.

Using a microsyringe, a measured amount of the working solution was placed in the well of the vaporizing chamber. A silver wool plug was inserted in the entrance end of the assembly and air was drawn through at a rate of 100 ml per minute. After 10 minutes the heating tape was activated and adjusted to give a temperature of 150 C to sublime the (dried) $HgCl_2$ remaining in the tube. The run was continued for an additional 20 minutes after which the collected mercury was determined in the usual manner. The results obtained from seven separate runs are shown in Table 16. These data indicate that the pyrolyzer is effective in releasing mercury vapor from $HgCl_2$ particulates.

Collection of Mercury From $(CH_3)_2Hg$ Using Pyrolyzer at Several Temperatures

A standard stock solution of dimethyl mercury was prepared by dissolving 114 mg of $(CH_3)_2Hg$ in 500 ml of alcohol to give a solution containing 198.3 µg Hg per ml. A standard working solution was prepared by diluting 1.0 ml of the stock solution to 100 ml with alcohol, giving a solution containing 1.983 µg Hg per ml.

TABLE 16. COLLECTION OF MERCURY FROM $HgCl_2$ PARTICULATE USING PYROLYZER

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
9	7.77	100	90	
9	8.98	100	109	
9	7.98	100	93	
9	8.25	100	97	
9	4.35	50	47	
9	4.69	50	50	
9	1.93	20	20	97.0

A series of runs were made using the vaporizer-pyrolyzer assembly shown in Figure 13. In each run a measured amount of the working solution was placed in the vaporizer by means of a microsyringe. The flow rate was controlled at 100 ml per minute and continued for 30 minutes. At the end of each run the collector was removed and the collected mercury was determined in the usual manner. The results of runs made with pyrolyzer temperatures of 500°C, 550°C, and 600°C are shown in Table 17. The average recovery of mercury at each pyrolyzer temperature was more than 100 percent. These data indicate no significant differences in pyrolyzer efficiency over the temperature range of 500°C to 600°C.

Construction Details of the Pyrolysis Tube and Furnace

Details of the pyrolysis tube and heating unit used in the studies reported above are shown in Figure 14. Since the data indicate that close temperature control may not be necessary to obtain reliable results, a simple step-down transformer might be used as a power supply for a field-test unit. However, the varying heat losses which may be encountered in field testing situations have not been determined. Some changes in the amount and type of insulation may be necessary to accommodate all conditions.

DISCUSSION AND CONCLUSION

This research program dealt primarily with two systems for the collection and analysis of mercury collected from ambient air. The first method utilizes a solution of ICl and was chosen by EPA for study because at the initiation of the program it appeared to be the best of the existing methods. This judgment was confirmed by the current research program. With proper care, principally in maintaining relatively low air flows, the collection of mercury and (at least some) of its compounds is quantitative. This fact alone makes the ICl solution system unique and valuable.

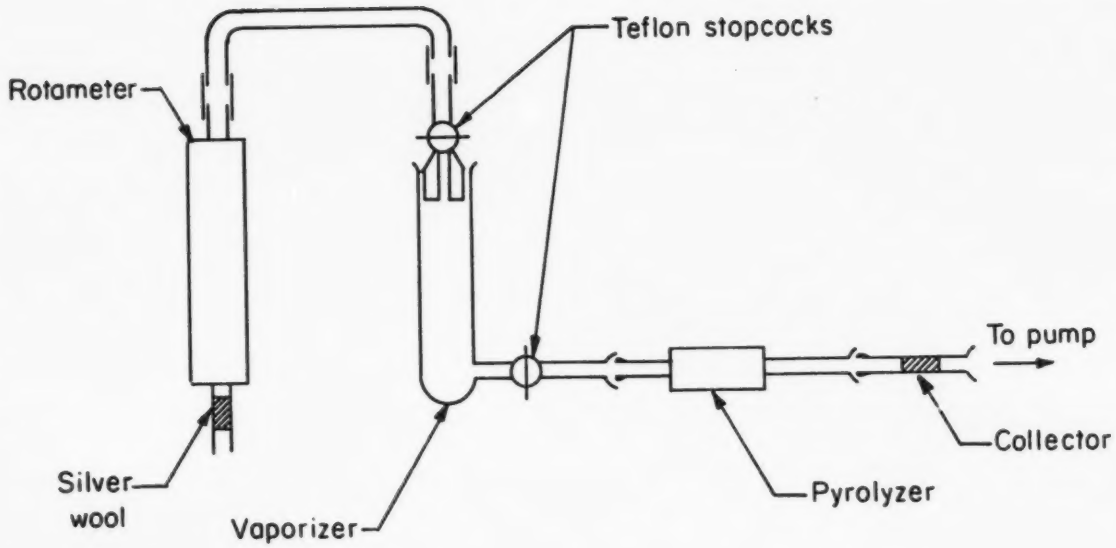

FIGURE 13. VAPORIZER-PYROLYZER ASSEMBLY

TABLE 17. COLLECTION OF MERCURY FROM $(CH_3)_2Hg$ USING PYROLYZER

Run No. 1 - Pyrolyzer Temperature = 600 °C

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
6	9.37	99.2	115	
9	8.39	99.2	100	
10	9.09	99.2	111	
11	8.74	99.2	105	109.0
9	4.76	49.6	51	
10	4.76	49.6	51	
9	4.73	49.6	51	
6	4.93	49.6	53	104.0
10	2.02	19.8	21	
9	2.03	19.8	21	
10	2.00	19.8	21	106.0

Run No. 2 - Pyrolyzer Temperature = 550 C

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
9	4.88	49.6	53	
4	9.44	99.2	114	
9	2.03	19.8	21	111.0

Run No. 3 - Pyrolyzer Temperature = 500 C

Collector	Peak Area, $mm^2 \times 10^{-2}$	Hg Added, Nanograms	Hg Found, Nanograms	Average Recovery, Percent
4	2.01	19.8	21	
9	8.64	99.2	103	
4	4.86	49.6	52	
11	5.04	49.6	54	
4	8.83	99.2	106	106.0

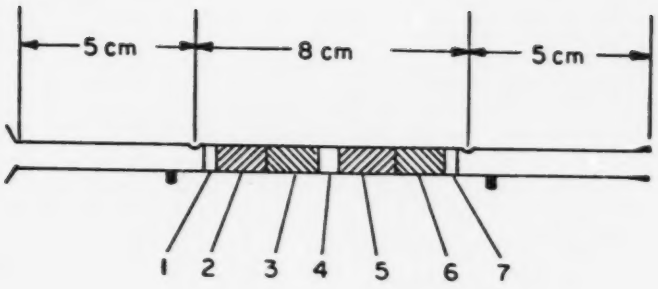

FIGURE 14. PYROLYSIS TUBE

Tube: 7-mm ID Vycor with 12/5 ball joints.

Tube Packing

(1) Quartz wool - small plug
(2) Copper oxide - 0.5 g
(3) Silver tungstate/MgO - 0.4 g
(4) Silver wool - 0.5 g
(5) Silver tungstate/MgO - 0.4 g
(6) Copper oxide - 0.5 g
(7) Quartz wool - small plug

Heating zone wrapped with 150 cm of 22-gage Chromel A wire and covered with asbestos to provide 1.2-cm insulation. With this configuration a current of about 5 A (20 VAC input, 100 watts) through the Chromel A wire heats the tube packing to 600 ± 25 C under laboratory conditions.

Analytical procedures to determine the mercury collected by ICl have been developed and are reasonably reliable. A dithizone extraction method is not recommended from the standpoint of accuracy and reliability at low mercury levels; it also suffers from the disadvantage of being slow and tedious. Double aeration, if carefully practiced, gives good results; but poor recovery is noted occasionally, with no apparent explanation. Apart from the extra time required for two aerations, the method is generally satisfactory.

Were it not for the method discussed below, the ICl solution collection scheme would be the logical candidate for additional study, and perhaps for adoption as the preferred means to collect total atmospheric mercury.

The method that, in experiments described in this report, has proven superior to the ICl collection system is based upon the collection of mercury (Hg^{o}) vapor on silver wool. For total atmospheric mercury collection, the collector is preceded by a catalytic pyrolysis furnace that converts inorganic particulates ($HgCl_2$) and organometallics [$(CH_3)_2Hg$] to Hg^{o}. Based on the studies reported here, using these two mercury compounds, the system is well-suited for its intended purpose, total mercury collection. Furthermore, common gaseous pollutants that might be suspected poisons for the silver wool collector have been shown to produce no appreciable lessening in the collection efficiency. Finally, the mercury is collected in a form (silver amalgam) readily adaptable to the rapid flameless atomic absorption analysis for mercury. Considering these facts, the pyrolysis-silver wool system appears, at this time, to be the method of choice for total mercury collection.

FUTURE WORK

It is recommended, that several aspects of the two major systems receive additional attention.

(1) Iodine monochloride system. A fundamental study is needed to clarify the chemistry involved in the collection of mercury compounds and the subsequent release of mercury. The role of complex ions should be understood. The kinetics of absorption (complex formation?) appeared in this program to be a probable cause of incomplete recovery, but the data were not definitive. If ICl is chosen as a primary or back up (referee) method for total mercury collection, these basic studies should be made.

The actual analysis appears satisfactory and improvements should be in time and cost efficiency, with perhaps some work being directed toward making the aeration method completely reliable.

(2) Pyrolysis and silver wool collection. This collection method offers the most promise at this time. A proposal has been submitted to EPA in reply to RFP DU-72-B406 to develop a prototype instrument for field collection of atmospheric mercury. This proposal is based on the pyrolysis-silver wool system and acknowledges the source (Drs. Thompson and Scott) of the concept. If accepted by EPA, the work proposed should answer most of the remaining questions about the validity of the pyrolysis-silver wool method.

REFERENCES

(1) Chase, Dan L., Huber, Frank E., and Henry, William M., "Development and Evaluation of an Analytical Method for the Determination of Total Atmospheric Mercury", Contract No. EHSD 71-32, Environmental Protection Agency.
- First Monthly Report, December 28, 1970.

(2) - Second Monthly Report, January 26, 1971.

(3) - Third Monthly Report, February 26, 1971.

(4) - Fourth Monthly Report, March 26, 1971.

(5) - Fifth Monthly Report, April 27, 1971.

(6) - Sixth Monthly Report, May 26, 1971.

(7) - Seventh Monthly Report, June 15, 1971.

(8) - Eighth Monthly Report, July 22, 1971.

(9) - Ninth Monthly Report, August 26, 1971.

(10) - Tenth Monthly Report, September 29, 1971.

(11) - Eleventh Monthly Report, October 25, 1971.

(12) - Twelfth Monthly Report, November 30, 1971.

(13) - Thirteenth Monthly Report, December 22, 1971.

(14) - Fourteenth Monthly Report, February 2, 1972.

(15) - Fifteenth Monthly Report, February 25, 1972.

(16) - Summary Report, September 2, 1971.

(17) Chase, Dan L., Henry, William M., and Sgontz, D. L., "Development and Evaluation of an Analytical Method for the Determination of Total Atmospheric Mercury", Contract No. EHSD 71-32, Environmental Protection Agency.
- First Progress Report, Phase IV, March 20, 1972.

(18) - Second Progress Report, Phase IV, March 24, 1972.

(19) - Third Progress Report, Phase IV, April 4, 1972.

(20) Linch, A. L., Stalzer, R. F., and Lefferts, D. T., "Methyl and Ethyl Compounds - Recovery From Air And Analysis", Am. Ind. Hygiene Assoc. J. 29 (No. 1), 79 (1968).

REFERENCES (Continued)

(21) O'Keefe, A. E. and Ortman, G. C., "Primary Standards fo Trace Gas Analysis", Anal. Chem. 32, p 760 (1966).

(22) Hatch, W. Ronald and Ott, Welland L., "Determination of sub-Microgram Quantities of Mercury by Atomic Absorption", Anal. Chem. 40 (No. 14), p 2085 (1968).

(23) Monkman, J. L., Mafett, Patricia A., and Doherty, T. F., "The Determination of Mercury in Air Samples and Biological Materials", Am. Ind. Hygiene Assoc. Quart. J. 17 (No. 4), p 418 (1956).